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Geonomics, Inc., Berkeley, CA

Prepared for

Environmental Monitoring and Support Lab., Las Vegas, NV

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Agency

Environmental Monitoring
and Support Laboratory
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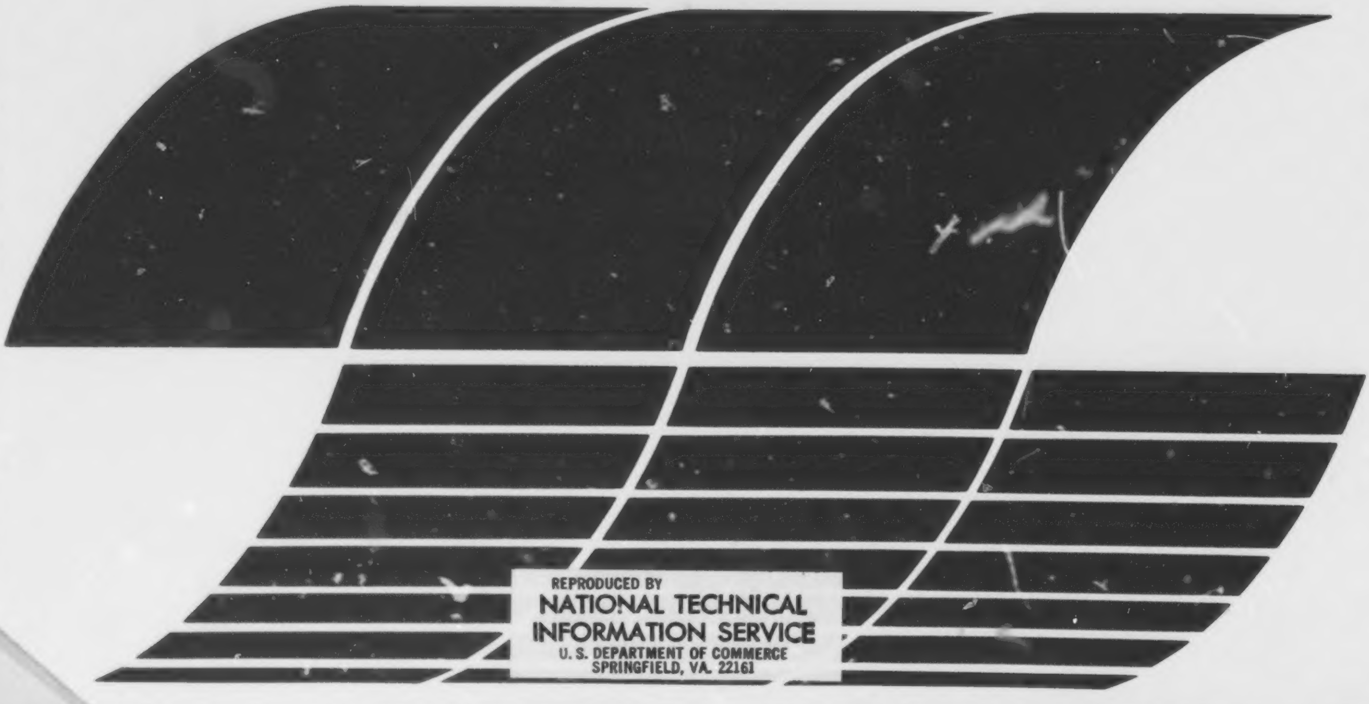
February 15-17, 1977
Las Vegas, Nevada

Interagency Energy-Environment Research and Development Program Report



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This report has been assigned to the INTERAGENCY ENERGY—ENVIRONMENT RESEARCH AND DEVELOPMENT series. Reports in this series result from the effort funded under the 17-agency Federal Energy/Environment Research and Development Program. These studies relate to EPA'S mission to protect the public health and welfare from adverse effects of pollutants associated with energy systems. The goal of the Program is to assure the rapid development of domestic energy supplies in an environmentally-compatible manner by providing the necessary environmental data and control technology. Investigations include analyses of the transport of energy-related pollutants and their health and ecological effects; assessments of, and development of, control technologies for energy systems; and integrated assessments of a wide range of energy-related environmental issues.

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EPA-600/7-78-121
June 1978

PROCEEDINGS

OF THE

SECOND WORKSHOP ON SAMPLING GEOTHERMAL EFFLUENTS

February 15-17, 1977
Las Vegas, Nevada

Sponsored by

Environmental Monitoring and Support Laboratory
Las Vegas, Nevada
Industrial Environmental Research Laboratory
Cincinnati, Ohio
Office of Energy, Minerals and Industry
Washington, D.C.
of the
U.S. Environmental Protection Agency

prepared by

Geonomics, Inc.
3165 Adeline Street
Berkeley, California 94703

Contract No. 68-03-2468

Project Officer

Donald B. Gilmore
Environmental Monitoring and Support Laboratory
Las Vegas, Nevada 89114

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89114

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FOREWORD

Protection of the environment requires effective regulatory actions which are based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of specific pollutants in the environment requires a total systems approach which transcends the media of air, water, and land. The Environmental Monitoring and Support Laboratory-Las Vegas contributes to the formation and enhancement of a sound monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs

This report contains the Proceedings of the Second Workshop on Sampling Geothermal Effluents. Collectively, the papers presented here provide much insight into the complex subject of geothermal effluent sampling. It is hoped that these Proceedings prove of value in helping to continue an exchange of ideas among those involved in the development of geothermal resources. For further information on this and future workshops on this subject, contact the Monitoring Systems Design and Analysis Staff (MSA) of the Environmental Monitoring and Support Laboratory, Las Vegas, Nevada.

The Environmental Monitoring and Support Laboratory-Las Vegas wishes to take this opportunity to express its appreciation and gratitude to those organizations and persons who gave so freely of their time and resources to make this workshop a success.

George B. Morgan

George B. Morgan
Director
Environmental Monitoring and Support Laboratory
Las Vegas

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Not all the papers presented at the Workshop were received in time for publication in these proceedings. They are listed in the Program, but not in the Contents. Those papers for which only an abstract was received are marked with an asterisk (*) in the Contents. These abstracts are included in this proceedings document.

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Second Workshop on
SAMPLING AND ANALYSIS OF GEOTHERMAL EFFLUENTS

February 15-17, 1977
Las Vegas, Nevada

Sponsored by

Environmental Monitoring and Support Laboratory
Las Vegas, Nevada

Industrial Environmental Research Laboratory
Cincinnati, Ohio

Office of Energy, Minerals, and Industry
Washington, D. C.

of the

U. S. Environmental Protection Agency

PROGRAM

Tuesday, 15 February

Introductory Session

9:00 - 9:10 a.m.	WELCOME ADDRESS G. B. Morgan, EMSL, U.S. EPA, Las Vegas, Nevada
9:10 - 9:25 a.m.	NEED FOR STANDARD METHODOLOGIES IN GEOTHERMAL EFFLUENT SAMPLING AND ANALYSIS A. C. Trakowski, Jr., Office of Monitoring and Technical Support, U.S. EPA, Washington, D. C.
9:25 - 9:40 a.m.	THE ROLE OF EPA'S INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY IN GEOTHERMAL DEVELOPMENT R. P. Hartley, IERL, U.S. EPA, Cincinnati, Ohio
9:40 - 9:55 a.m.	ERDA'S ROLE IN GEOTHERMAL ENVIRONMENTAL IMPACT RESEARCH A. Jelacic, Division of Geothermal Energy, U.S. ERDA, Washington, D. C.
9:55 - 10:10 a.m.	ELECTRICAL POWER RESEARCH INSTITUTE ROLE IN GEOTHERMAL ENVIRONMENTAL IMPACT RESEARCH V. W. Roberts, EPRI, Palo Alto, California

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Geonomics, Inc.
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For further information, contact Donald B. Gilmore, Project Officer, (702)736-2969, ext. 241, in Las Vegas.

16. ABSTRACT

This is a compilation of papers presented at the second in a series of workshops on sampling and analysis of geothermal effluents held February 15-17, 1977, at Las Vegas, Nevada. The purpose of this workshop was to continue the exchange of ideas and knowledge initiated in the first workshop of October 1975 with the intent of eventually developing an acceptable set of standard geothermal effluent sampling and analysis methods. Thirty-one papers were presented by representatives of industry, universities and government. All of the abstracts and 17 of the papers are published in this document.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Monitors	Geothermal energy	13B
Pollution	Methods development	14A
Sampling		14B
Analysis		14C
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10:10 - 10:30 a.m.	COFFEE
	Gas Sampling and Analysis Session Session Chairman: P. Kruger, Stanford University, Stanford, California
10:30 - 10:55 a.m.	THE USE OF GAS SAMPLING BAGS FOR THE COLLECTION AND STORAGE OF HYDROTHERMAL GASES A. J. Soinski, LFE Corporation, Richmond, California
10:55 - 11:20 a.m. (paper withdrawn)	SOURCE TERM ANALYSIS OF NON-CONDENSIBLE GASES IN THE IMPERIAL VALLEY -- MEASUREMENT METHODOLOGY AND RESULTS P. Phelps, Lawrence Livermore Laboratory, Livermore, California
11:20 - 11:45 a.m.	HEAVY METAL EMISSIONS FROM GEOTHERMAL POWER PLANTS D. E. Robertson, Battelle-Northwest Laboratories, Richland, Washington
11:45 - 12:10 p.m.	THE DYNAMIC MEASUREMENT OF AMBIENT AIRBORNE GASES NEAR GEOTHERMAL AREAS A. F. Jepsen, Eureka Resource Associates, Incorporated, Berkeley, California, and L. Langan, Environmental Measurements, Incorporated, San Francisco, California
12:10 - 1:40 p.m.	LUNCH
	Noble Gases Session Session Chairman: R. P. Hartley, IERL, U.S. EPA, Cincinnati, Ohio
1:40 - 2:05 p.m.	ANALYSIS OF RADON IN GEOTHERMAL EFFLUENTS P. Kruger, Civil Engineering Department, Stanford University, Stanford, California
2:05 - 2:30 p.m. (paper withdrawn)	RADON MEASUREMENTS AT THE GEYSERS P. Phelps, Lawrence Livermore Laboratory, Livermore, California
2:30 - 2:55 p.m.	NOBLE GAS SAMPLING OF THE GEOTHERMAL HEAT LOOP AT NILAND FIELD, CALIFORNIA M. O'Connell, ORP, U.S. EPA, Las Vegas, Nevada

	Sulfide Session Session Chairman: D. B. Gilmore, EMSL, U.S. EPA, Las Vegas, Nevada
2:55 - 3:20 p.m.	A REVIEW OF THE DETERMINATION OF HYDROGEN SULFIDE IN AIR BY THE CADMIUM HYDROXIDE-STRACTAN COLORIMETRIC METHOD: CURRENT PRACTICES AND MODIFICATIONS R. A. McCurdy and S. L. Altshuler, Pacific Gas & Electric, San Ramon, California
3:20 - 3:40 p.m.	COFFEE
3:40 - 4:05 p.m.	THE MEASUREMENT AND DISTRIBUTION OF GEOTHERMAL SULFUR POLLUTANTS IN THE GEYSERS AREA L. A. Cavanagh, Stanford Research Institute, Menlo Park, California
4:05 - 4:20 p.m.	FIELD DETERMINATION OF TOTAL SULFIDES G. Frye and D. W. Wheeler, Aminoil USA, Incorporated, Santa Rosa, California
4:20 - 4:35 p.m. (paper withdrawn)	AMBIENT H_2S MEASUREMENTS IN THE IMPERIAL VALLEY P. Phelps or alternate, Lawrence Livermore Laboratory, Livermore, California
4:35 - 5:35 p.m.	PANEL DISCUSSION Chairman: V. W. Roberts, EPRI, Palo Alto, California Topic: "Gas Sampling and Analysis"
5:35 - 6:35 P.M.	NO HOST COCKTAIL
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	General Sampling & Analysis Session Session Chairman: B. Wiersma, EMSL, U.S. EPA, Las Vegas, Nevada
9:00 - 9:25 a.m.	CHEVRON PLANS FOR ON-SITE SAMPLING AND ANALYSING OF GEOTHERMAL WATERS W. J. Subcasky, Chevron Oil Field Research Company, La Habra, California
9:25 - 9:50 a.m.	DEVELOPMENT OF A STANDARD METHODS MANUAL FOR SAMPLING AND ANALYSIS OF GEOTHERMAL FLUIDS AND GASES E. M. Woodruff, Battelle-Northwest Laboratories, Richland, Washington

9:50 - 10:15 a.m.	SAMPLING AND CHARACTERIZATION OF SUSPENDED SOLIDS IN BRINE FROM MAGMAMAX #1 WELL J. H. Hill, Lawrence Livermore Laboratory, Livermore, California
10:15 - 10:35 a.m.	COFFEE
10:35 - 11:00 a.m.	SAMPLING AND ANALYSIS OF HOT AND COLD SPRING WATERS AND ASSOCIATED ROCK AND SOIL SAMPLES FROM POTENTIAL GEOTHERMAL RESOURCES AREAS IN NORTH CENTRAL NEVADA H. R. Bowman, H. Wollenberg, F. Asaro and A. Hebert, Lawrence Berkeley Laboratory, Berkeley, California
11:00 - 11:25 a.m.	METHODOLOGY FOR SAMPLING AND ANALYSIS OF HIGH PRESSURE STEAM LINES W. Hamersma, TRW Incorporated, Redondo Beach, California
11:25 - 11:45 a.m.	HOW CAN STANDARD METHODS FOR SAMPLING AND ANALYSIS SUPPORT THE MOTIVES BEHIND THE REGULATIONS? D. E. Michels, EG&G Idaho, Incorporated, Idaho Falls, Idaho
11:45 - 12:00 p.m.	A REVIEW OF THE CHEMICAL COMPOSITION OF GEOTHERMAL EFFLUENTS F. Tsai, S. Juprasert and S. K. Sanyal, Geonomics, Incorporated, Berkeley, California
12:00 - 12:15 p.m. (paper withdrawn)	GEOTHERMAL SAMPLING AND ANALYSIS EXPERIENCE IN EL SALVADOR G. Cuellar and J. Molina, Comisión Eléctrica Río Lempa, Soyapango, El Salvador
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1:45 - 2:10 p.m. (paper withdrawn)	GEOTHERMAL WATER SAMPLING IN THE IMPERIAL VALLEY --WHAT, WHERE, AND HOW TO MEASURE P. Phelps, Lawrence Livermore Laboratory, Livermore, California
2:10 - 2:35 p.m.	DEVELOPMENT OF GEOTHERMAL GAS SAMPLING EQUIPMENT F. B. Tonani, Geochemex, Incorporated, Berkeley, California

2:35 - 3:00 p.m.	SAMPLING FOR RESERVOIR FLUID RECONSTRUCTION M. J. Reed, U. S. Geological Survey, Menlo Park, California
3:00 - 3:25 p.m.	TECHNIQUES OF PRESSURE AND TEMPERATURE MEASUREMENT AND SAMPLING IN GEOTHERMAL WELLS L. W. Ross, L. L. Brown and R. E. Williams, Denver Research Institute, Denver, Colorado
3:25 - 3:45 p.m.	COFFEE
3:45 - 4:10 p.m.	COLLECTION AND ANALYSES OF GAS AND ISOTOPE SAMPLES FROM GEOTHERMAL WELLS N. L. Nehring and A. H. Truesdell, U. S. Geological Survey, Menlo Park, California
4:10 - 4:35 p.m.	GEOTHERMAL DOWNHOLE SAMPLING INSTRUMENTATION R. Fournier and J. M. Thompson, U. S. Geological Survey, Menlo Park, California
4:35 - 5:35 p.m.	PANEL DISCUSSION Chairman: E. Bretthauer, EMSL, U.S. EPA, Topic: "Liquid Sampling and Analysis"
Thursday, 17 February	
	Analytical Methods, Results, Interpretation Session Session Chairman: C. Wayman, Region VIII, U.S. EPA, Denver, Colorado
9:00 - 9:25 a.m. (talk cancelled)	ANALYSIS OF TRACE CONTAMINANTS IN LOW TO MEDIUM SALINITIES GEOTHERMAL FLUIDS K. Y. Chen, Environmental Engineering Program, University of Southern California, Los Angeles, California
9:25 - 9:50 a.m.	CASE HISTORY OF GEOTHERMAL EFFLUENT SAMPLING FOR FOUR GEOTHERMAL WELLS G. R. Conner and P. B. Needham, Jr., College Park Metallurgy Research Center, U. S. Bureau of Mines, College Park, Maryland

9:50 - 10:15 a.m.	ESTIMATION OF POLLUTANT CHARACTERISTICS FROM GEOCHEMICAL SURFACE INVESTIGATIONS F. B. Tonani, Geochemex, and H. T. Meidav, Geonomics, Incorporated, Berkeley, California
10:15 - 10:35 a.m.	COFFEE
10:35 - 11:00 a.m.	SAMPLING AND ANALYSIS OF GEOTHERMAL BRINES FROM NILAND FIELD, CALIFORNIA H. K. Bishop, San Diego Gas & Electric Company, San Diego, California
11:00 - 11:25 a.m.	INTERPRETATION OF ANALYTICAL RESULTS THERMAL AND NON-THERMAL WATERS, LAVA PLATEAUS REGION OF NORTHEASTERN CALIFORNIA AND SOUTHERN OREGON C. W. Klein and J. B. Koenig, GeothermEx, Incorporated, Berkeley, California
11:25 - 11:50 a.m.	GEOCHEMICAL ANALYSIS OF FLUIDS CIRCULATED THROUGH A GRANITIC HOT DRY ROCK GEOTHERMAL SYSTEM J. W. Tester, C. Grigsby, C. Holley and L. Blatz, Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico
11:50 - 12:15 p.m.	CHEMICAL PROFILE OF THE EAST MESA GEOTHERMAL FIELD, IMPERIAL VALLEY, CALIFORNIA R. T. Littleton and E. Burnett, U. S. Bureau of Reclamation, Boulder City, Nevada
12:15 - 1:45 p.m.	LUNCH
	Related Topics Session Session Chairman: R. Littleton, U. S. Bureau of Reclamation, Boulder City, Nevada
1:45 - 2:10 p.m.	STATUS REPORT, RAFT RIVER PROJECT, SAMPLING, ANALYSIS, AND ENVIRONMENTAL EFFECTS STUDIES A.C. Allen, J.M. Baldwin and R.E. McAtee, Allied Chemical Corp., Idaho Falls, Idaho
2:10 - 2:35 p.m.	BOREHOLE GEOPHYSICAL LOGGING AS COMPLEMENT TO GEOTHERMAL WELL EFFLUENT SAMPLING S. K. Sanyal and R. B. Weiss, Geonomics, Incorporated, Berkeley, California

2:35 - 3:00 p.m.	USE OF RADIOACTIVE TRACERS IN GEOTHERMAL OPERATIONS O. Vetter, Vetter Associates, Laguna Beach, California
3:00 - 3:25 p.m.	THE LBL GEOTHERMAL BRINE DATA COMPILATION PROJECT S. R. Cosner and J. A. Apps, Lawrence Berkeley Laboratory, Berkeley, California
3:25 - 3:45 p.m.	COFFEE
3:45 - 5:00 P.M.	WRAP-UP PANEL DISCUSSION Chairman: D. B. Gilmore, EMSL, U.S. EPA, Las Vegas, Nevada

LIST OF REGISTERED PARTICIPANTS

1. William Adams
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

2. John A. Apps
Building 90-2130
Lawrence Berkeley Laboratory
Berkeley, California 94720

3. Harry G. Arnold
P. O. Box X
Building 4500N, D-33
Oak Ridge, Tennessee 37830

4. Dr. David J. Atkinson
Hydro-Search, Incorporated
333 Flint Street
Reno, Nevada 89501

5. L. H. Axtell
Geothermal Services, Incorporated
7860 Convoy Court
San Diego, California 92111

6. Allan R. Batterman
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

7. Harry Bishop
San Diego Gas & Electric Company
P. O. Box 1831
San Diego, California 92112

8. Robert Boshan
Hughes Aircraft Company
2012 Midvale Avenue
Los Angeles, California 90025

9. Harry R. Bowman
Building 70-189
Lawrence Berkeley Laboratory
Berkeley, California 94720

10. Erich Bretthauer
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

11. Charles Brook
U.S. Geological Survey
345 Middlefield Road
Menlo Park, California 94025

12. Ken W. Brown
U.S. EPA, EMSL
5127 Blanton Drive
Las Vegas, Nevada 89122

13. Larry L. Brown
University of Denver
1442 South Vivian Way
Lakewood, Colorado 80215

14. Dwight Lee Carey
Republic Geothermal, Incorporated
11823 East Slauson, Suite 1
Santa Fe Springs, California 90670

15. Harry M. Castrantas
FMC Corporation
407 South Norwood Avenue
Newton, Pennsylvania 18940

16. Leonard A. Cavanagh
Stanford Research Institute
1550 Calaveras Avenue
San Jose, California 95126

17. Raymond Cedillo
Southern California Edison Company
9329 Glendon Way
Rosemead, California 91770

18. Donald J. Christoffersen
Union Oil Company
P. O. Box 76
Brea, California 92621

19. Gerald Conner
U.S. Bureau of Mines
College Park Metallurgy Research Center
College Park, Maryland 20740

20. Steven R. Cosner
Building 90-2024P
Lawrence Berkeley Laboratory
Berkeley, Califonia 94720

21. Glen Coury
Coury & Associates
7400 West 14th Avenue, Suite 2
Lakewood, Colorado 80214

22. Alan B. Crockett
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 98114

23. Gustavo Cuellar
Comisión Eléctrica Río Lempa
Calle Los Claveles-21
Col. La Sultana - Antiguo
Cuscatlan, El Salvador

24. Gene Culver
Geo-Heat Utilization Center
Oregon Institute of Technology
Klamath Falls, Oregon 97601

25. Lester Danterive
U.S. Geological Survey
345 Middlefield Road
Menlo Park, California 94025

26. Otis L. Day
Geonomics, Incorporated
3165 Adeline Street
Berkeley, California 94703

27. Frank Dellechaie
AMAX Exploration, Incorporated
4704 Harlan Street
Denver, Colorado 80212

28. Daniel A. Demeo
Hughes Aircraft Company
Building 6-D-133
Centinela and Teale Streets
Culver City, California 90230

29. Leo Deffending
Battelle-Northwest Laboratories
P. O. Box 999
Richland, Washington 99352

30. Sam Dermengian
Geothermal Energy Magazine
318 Cherrywood Street
West Covina, California 91741

31. Jay D. Dick
Denver Research Institute
University of Denver
Denver, Colorado 80208

32. Jane Dionne
Federal Energy Administration
1200 Pennsylvania Avenue, Northwest
Washington, D. C. 20461

33. Gene Elliott
Federal Bureau of Mines
1605 Evans Avenue
Reno, Nevada 89512

34. Giancarlo Facca
1023 Timothy Lane
Lafayette, California 94549

35. Wayne A. Fernelius
Bureau of Reclamation
P. O. Box 427
Boulder City, Nevada

36. Bill Fiero
University of Nevada
4505 Maryland Parkway South
Las Vegas, Nevada 89154

37. Peter Fintschenko
FMC Corporation
2000 Market Street
Philadelphia, Pennsylvania 19103

38. Carl Flegal
TRW, Incorporated
01-2030, One Space Park
Redondo Beach, California 90278

39. Jack F. Foehr
CER Corporation
P. O. Box 15090
Las Vegas, Nevada 89114

40. Gary W. Frey
U. S. Bureau of Reclamation
310 Wyoming Street
Boulder City, Nevada 89005

41. George A. Frye
Aminoil USA, Incorporated
P. O. Box 11279
Santa Rosa, California 95406

42. John Fruchter
Battelle-Northwest Laboratories
P. O. Box 999
Richland, Washington 99352

43. Murray C. Gardner
GeothermEx, Incorporated
901 Mendocino Avenue
Berkeley, California 94707

44. Donald B. Gilmore
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

45. Louis H. Goldsmith
Geonomics, Incorporated
Apartado 2475
Managua, Nicaragua

46. Paul Gudiksen
Lawrence Livermore Laboratory
P. O. Box 808
Livermore, California 94550

47. M. S. Gulati
Union Oil Company
P. O. Box 6854
Santa Rosa, California 95405

48. W. Roger Hail
W. A. Wahler & Associates
1023 Corporation Way
Palo Alto, California 94303

49. Beverly A. Hall
Geothermal Resources Council
P. O. Box 1033
Davis, California 95616

50. J. Warren Hamersma
TRW Defense & Space Systems
01-2020, One Space Park
Redondo Beach, California 90278

51. Robert P. Hartley
U.S. EPA, IERL
5555 Ridge Avenue
Cincinnati, Ohio 45268

52. Jonathan Herrmann
U.S. EPA, Region VIII
1860 Lincoln Street, Suite 900
Denver, Colorado 80011

53. John H. Hill
Lawrence Livermore Laboratory
P. O. Box 808, L-404
Livermore, California 94550

54. Anders F. Jepsen
Eureka Resource Associates, Incorporated
2161 Shattuck Avenue, Suite 317
Berkeley, California 94704

55. Richard L. Jodry
Suntech, Incorporated
P. O. Box 936
Richardson, Texas 75080

56. F. B. Johns
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

57. Stuart D. Johnson
Phillips Petroleum Company
P. O. Box 752
Del Mar, California 92014

58. Robert Kent
U.S. Geological Survey
345 Middlefield Road
Menlo Park, California 94025

59. Christopher W. Klein
GeothermEx, Incorporated
901 Mendocino Avenue
Berkeley, California 94707

60. William T. Kreiss
Physical Dynamics, Incorporated
5737 37th Avenue Northeast
Seattle, Washington 98105

61. Paul Kruger
Civil Engineering Department
Stanford University
Stanford, California 94305

62. Robert T. Littleton
U.S. Bureau of Reclamation
624 Don Vincente Drive
Boulder City, Nevada 89005

63. Carlos V. Lopez
Empresa Nacional de Luz & Fuerza
Altamira d'Este 317
Managua, Nicaragua

64. J. D. Ludwick
Battelle-Northwest Laboratories
1616 Woodbury
Richland, Washington 99352

65. Bruce Mann
U.S. EPA, ORP
P. O. Box 15027
Las Vegas, Nevada 89114

66. Skip Matlick
Republic Geothermal, Inc.
P. O. Box 3388
Santa Fe Springs, California 90670

67. R. E. McAtee
Allied Chemical Corporation
550 2nd Street
Idaho Falls, Idaho 83401

68. Richard McCurdy
Pacific Gas & Electric
3400 Crow Canyon Road
San Ramon, California 94583

69. Katherine F. Meadows
Geothermal World Directory
P. O. Box 997
Glendora, California 91740

70. H. Tsvi Meidav
Geonomics, Incorporated
3165 Adeline Street
Berkeley, California 94703

71. Mae Z. Meidav
Geonomics, Incorporated
3165 Adeline Street
Berkeley, California 94703

72. Donald E. Michels
EG&G Idaho, Incorporated
307 2nd Street
Idaho Falls, Idaho 83401

73. Leland L. Mink
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

74. Jorge R. Molina
Comisión Eléctrica Río Lempa
31 Av. Sur #209 Col Cucumacryan
San Salvador, El Salvador

75. Robert E. Moran
U.S. Geological Survey
M. S. 415, Federal Center
Denver, Colorado 80215

76. George B. Morgan
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

77. Gió M. Morse
Geonomics, Incorporated
3165 Adeline Street
Berkeley, California 94703

78. John G. Moylan
Lockheed Electric Company
4220 South Maryland Parkway
Las Vegas, Nevada 89109

79. David A. Myers
Battelle-Northwest Laboratories
2533 Davison
Richland, Washington 99352

80. Nancy L. Nehring
U.S. Geological Survey
345 Middlefield Road
Menlo Park, California 94025

81. Peter O. Nelson
Department of Civil Engineering
Oregon State University
Corvallis, Oregon 97331

82. Zachary Nelson
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

83. Charles Otto
Lawrence Livermore Laboratory
Box 808, L-404
Livermore, California 94550

84. Alan O. Ramo
Sunoco Energy Development Company
12700 Park Central Place, Suite 1500
Dallas, Texas 75251

85. Kenneth Rea
Los Alamos Scientific Laboratory
P. O. Box 1663
Los Alamos, New Mexico 87545

86. Marshall Reed
U.S. Geological Survey, MS 92
345 Middlefield Road
Menlo Park, California 94025

87. Jerry A. Richl
Northwest Environmental Technical Laboratories,
Incorporated
5709 80th Avenue Southeast
Merrer Island, Washington 98040

88. David E. Robertson
Battelle-Northwest Laboratories
P. O. Box 999
Richland, Washington 99352

89. Stephen Ronshaugen
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

90. L. W. Ross
Denver Research Institute
University of Denver
Denver, Colorado 80208

91. Subir K. Sanyal
Geonomics, Incorporated
3165 Adeline Street
Berkeley, California 94703

92. David Sarkaria
Aminoil USA, Incorporated
P. O. Box 191
Huntington Beach, California

93. Lew Schalit
Acurex-Aerotherm
485 Clyde Avenue
Mountain View, California 94042

94. Arthur J. Soinski
LFE Corporation
2030 Wright Avenue
Richmond, California 94804

95. Richard E. Stanley
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

96. William P. Staub
Oak Ridge National Laboratory
P. O. Box X, 4500N, D-33
Oak Ridge, Tennessee 37830

97. Beverly Strisower
Lawrence Berkeley Laboratory
Building 90-3081
Berkeley, California 94720

98. Wayne J. Subcasky
Chevron Oil Field Research Company
P. O. Box 446
La Habra, California 90631

99. Glenn Suter
Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

100. William Sutton
U.S. EPA, EMSL
P. O. Box 15027
Las Vegas, Nevada 89114

101. Chandler A. Swanberg
Department of Physics, Box 30
New Mexico State University
Las Cruces, New Mexico 88003

102. Jefferson W. Tester
Los Alamos Scientific Laboratory
Mail Stop 981
Los Alamos, New Mexico 87545

103. J. M. Thompson
U.S. Geological Survey
345 Middlefield Road
Menlo Park, California 94025

104. Franco B. Tonani
Geochemex, Incorporated
3165 Adeline Street
Berkeley, California 94703

105. Albert C. Trakowski
U.S. EPA, ORD
401 M. Street SW
Washington, DC 20460

106. Felix Tsai
Geochemex, Incorporated
3165 Adeline Street
Berkeley, California 94703

107. Otto Vetter
Vetter Associates
580 Vista Lane
Laguna Beach, California 92651

108. Jim Watson
Battelle-Northwest Laboratories
P. O. Box 999, Area 300, Building 314
Richland, Washington 99352

109. Cooper H. Wayman
U.S. EPA
1860 Lincoln, Suite 900
Denver, Colorado 80203

110. Richard B. Weiss
Geonomics, Incorporated
3165 Adeline Street
Berkeley, California 94703

111. Herbert C. Wells
Engineering Department
University of Nevada
4505 Maryland Parkway
Las Vegas, Nevada 89154

112. Robert N. Wheatley
Union Oil Company Research Center
1409 Skyline Drive
Fullerton, California 92631

113. D. W. Wheeler
Aminoil USA, Incorporated
P. O. Box 191
Huntington Beach, California 92648

114. Tricia White
Las Vegas Sun
P. O. Box 4275
Las Vegas, Nevada 89106

115. Barry Williams
7860 Convoy Court
San Diego, California 92111

116. Rod D. Wimer
Portland General Electric
121 Southwest Salmon
Portland, Oregon 97204

117. E. M. Woodruff
Battelle-Northwest Laboratories
P. O. Box 999
Richland, Washington 99352

118. Richard V. Wyman
Engineering Department
University of Nevada
4505 Maryland Parkway
Las Vegas, Nevada 89154

LIST OF ABBREVIATIONS AND SYMBOLS

µg/h or µg/hr = micrograms per hour
µg/l = micrograms per liter
µg/m or µg/min = micrograms per minute
µmho/cm = micromhos per centimeter

AA or AAS = atomic absorption spectrometer
atm = atmospheres

cc = cubic centimeter(s)
cm = centimeter(s)
CP-grade = chemically pure

DT = detector tube

ERDA = U.S. Energy Research and Development Administration
EPA = U.S. Environmental Protection Agency
e p m = equivalents per million

g or gm = gram(s)
g/m = grams per meter
g/m^3 = grams per cubic meter
GC = gas chromatograph
h or hr(s) = hour(s)
id, ID or i.d. = inside diameter
in = inch(es)
kg = kilogram(s)
KGRA = Known Geothermal Resource Area
km = kilometer(s)
lb = pound(s)
liq = liquid
lpm, l/m or l/min = liters per minute
mM/lt = millimoles per liter
mi = mile(s)

min = minute(s)
ml = milliliter
MV = megavolt
mV = millivolt
MW = megawatt

nm = nanometer(s)

od, OD or o.d. = outside diameter

ORP = oxidation-reduction potential
P log = pressure log
ppb = parts per billion
ppm = parts per million
ppt = parts per thousand
psi = pounds per square inch

SP log = self potential log
SpC = specific conductance

T log = temperature log
TDS = total dissolved solids
vap = vapor
V/V = volume per volume
wt = weight

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Pyrex Teflon
Tygon STRactan-10

METRIC CONVERSION TABLE

Non-metric unit	Multiply by	Metric unit
Fahrenheit	5/9(°F - 32)	Celsius
foot(feet)	0.3048	meter(s)
gallon(s)	3.7854	liter(s)
inch(es)	25.4	millimeter(s)
mile(s)	1.609	kilometer(s)
ounce	28.35	gram(s)
pound(s)	0.454	kilogram(s)
psi (pounds per square inch)	6894.7 0.06805	pascal(s) atmosphere(s)
ton(s)	0.9072	metric ton(s)

British units were used interchangeably in this document because much of the source data were not available in metric units.

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ABSTRACT

THE USE OF GAS SAMPLING BAGS FOR THE COLLECTION AND STORAGE OF HYDROTHERMAL GASES

A. J. Soinski
LFE Corporation
Environmental Analysis Laboratories
Richmond, California

The analysis of geothermal gas samples by means of gas chromatography or potentiometry is now routine and reliable. However, difficulties in the collection and storage of hydrothermal gases remain. The collected gas must be representative of the effluent, and sample modification by processes such as the reaction of component gases, contamination with ambient air, diffusional loss, or wall loss should not occur. In addition, it is desirable that the collection system be rugged, inexpensive, and easy to use. Gas sampling and storage bags, made from Tedlar, Teflon, or polyethylene film, have these latter convenience characteristics, but they may fail to meet the fundamental requirements for sample preservation.

We have performed some preliminary laboratory measurements of the stability of reactive and residual gases during storage in plastic bags. Sulfur-containing species are unstable, and they should be stabilized in aqueous solutions or on a solid matrix and/or analyzed on site. Diffusional losses of hydrogen are appreciable also. We conclude that the utility of plastic bags for the collection and storage of geothermal gases is limited to chemically stable and higher molecular weight species.

Solid adsorbents, such as silica gel and activated charcoal, are gaining favor over sampling bags for the collection of odorous gases in the workplace environment. The general requirements of component stability and freedom from contamination are fulfilled. We suggest that silica gel-filled adsorption tubes, similar to the one used for volcanic gases by Naughton, are preferable to plastic bags for geothermal gas collection and storage.

ABSTRACT

HEAVY METAL EMISSIONS FROM GEOTHERMAL POWER PLANTS

D. E. Robertson, E. A. Crecelius, J. S. Fruchter, J. D. Ludwick
Battelle-Northwest Laboratories, Richland, Washington

The high temperature magmatic processes which create the hydrothermal provinces of high geothermal energy potential also result in the accumulation of undesirable gases and liquids. During the tapping and utilization of geothermal fluids for power production, elevated levels of these naturally produced contaminants can be released to the surrounding environment. We have initiated a study to identify the quantities and chemical forms of volatile and water soluble heavy metals released in geothermal effluents. To date, our studies have been conducted at The Geysers, Cerro Prieto and Raft River geothermal sites.

Of the heavy metals studied, mercury is the most volatile, and gms/hour quantities are released from the generating units at The Geysers and Cerro Prieto. Mercury concentrations in Raft River steam and water are one to two orders of magnitude lower than at The Geysers and Cerro Prieto. The volatile mercury at all locations is predominantly elemental Hg^0 vapor, which was surprising because of the high concentrations of H_2S present.

Arsenic primarily follows the liquid phase at the hot water dominated sites and concentrations in the geothermal waters ranged from 28 μg/l in Raft River hot water to 2250 μg/l in the Cerro Prieto brine. At Cerro Prieto 2480 gms/hr of arsenic is released to an evaporation pond. At Cerro Prieto the arsenic in the fresh brine is primarily in the +3 oxidation state, but appears to oxidize rapidly to the +5 form when exposed to the atmosphere. The arsenic in fresh hot water from Raft River is initially present mainly in the +5 form.

THE DYNAMIC MEASUREMENT OF AMBIENT AIRBORNE GASES NEAR GEOTHERMAL AREAS

Anders F. Jepsen
Eureka Resource Associates, Inc.
Berkeley, California

and

Lee Langan
Environmental Measurements, Inc.
San Francisco, California

INTRODUCTION

In geothermal areas, as elsewhere, there are both man-made and natural sources of atmospheric contamination which are of interest from the point of view of either environmental impact or exploration. The most obvious are the clouds of smoke and steam from active volcanoes and the steam exhausts from operating geothermal power units, which can be seen for many miles. Less apparent but still of great human concern are the sulfide odors and mists from fumaroles and hot springs. Least obvious, in fact usually undetectable to the unequipped human (except for hydrogen sulfide) are the clouds of vapor emitted naturally in small but clearly measurable amounts by certain geological conditions as well as by development processes.

The assessment of the environmental impact caused by development of geothermal resources requires a quantitative distinction between the pre- and the post-development condition. In the past such a distinction has been difficult because of the lack of hard data, although that did not hinder some workers from assuming a zero level of contamination prior to development. Now, background data is a fundamental requirement in development programs in geothermal areas as well as elsewhere. Such data may be gathered by conventional means through pre-development stationary monitoring. They also may be obtained by such innovative methods as the dynamic measurement technique, in which clouds of air contaminant are *mapped* to define their measurable limits in space, that is, to background.

This paper will briefly describe the dynamic measurement technique and present some data obtained in this way from geothermal areas. Applications include not only environmental assessment but also geological reconnaissance.

THE DYNAMIC MEASUREMENT TECHNIQUE

The technique of dynamic measurement of air pollution has been applied on and off for many years, particularly to the study of specific source-oriented problems. Airborne measurements of plume gas concentrations have been made to try to verify emission rates and predictive model reliability. Ground-based dynamic measurements have been employed to trace suspected clouds of gas emitted by stationary sources, in response to complaints or to special scientific interest. All these efforts have been limited by the difficulty inherent in the slow-responding, delicate, chemical analyzers available for gas analysis. However, now that rugged, fast response air monitors which operate mostly on physical rather than chemical principles are available, the dynamic measurement technique is more widely used.

Dynamic air quality measurements are those which are made while the monitor is in motion, in contrast to static measurements, those traditionally made by a stationary monitor operating continuously at some location. The difference between static and dynamic measurement is that the stationary monitor waits for the air pollution to come to it while the moving monitor moves to the contaminating plume and measures it *in situ*. Because the dynamic measurements are made while the monitor is in motion, it is possible to map the distribution of the air pollution in both space and time. The data are both spatial and temporal in character. In contrast, the static measurement data are temporal only and contain no information as to location relative to the maximum concentration in the plume.

Meteorologists have been making dynamic measurements of the atmosphere for many years. The most familiar technique has been to measure the vertical wind profile, that is, the horizontal speed of the wind measured from the surface up to some elevation above the earth. This is accomplished by releasing a pilot balloon and tracking its movement through the atmosphere by means of a theodolite. Ultimately, from this set of measurements, the position of the balloon in space may be calculated as a function of time, and hence the horizontal wind speed determined as a function of altitude. Similar dynamic techniques can be used to measure pollutant profiles through atmospheric plumes to learn more about how they are dispersed and what levels of concentration actually prevail in them.

MOVING POINT ANALYZERS

To provide meaningful data in the moving mode, point analyzers must be able to meet strict specifications. They must be able to operate under varying conditions of temperature and humidity while experiencing the acceleration and shock common to vehicular operation.

Power demands should be low so several instruments can be used in the same system. The time response should be fast, on the order of a few seconds if possible, to maximize spatial resolution.

The time response is particularly important. The dynamic measurement procedure is specifically aimed at defining plume geometry and hence requires a measurement system which responds fast enough to sense and record gas levels at the plume edges, as well as at the point of maximum concentration.

Recent advances in air quality monitors make possible the dynamic measurement of several pollutants. The flame photometric detector and and pulsed fluorescent monitor both permit the accurate measurement of total sulfur of SO_2. The chemiluminescent method permits the accurate measurement of NO, NO_x, and O_3. A later section will discuss measurements made in a geothermal area using a Hg-sensitive spectrometer.

REMOTE SENSORS

Remote sensors provide a separate, unique approach in dynamic measurements. They are able to detect overhead clouds of gas without having to be in them,and their mode of operation permits moving measurements while they are themselves stationary. Passive remote sensors, such as the correlation spectrometer (COSPEC), rely on natural light from the sky as the source of energy and monitor the energy absorption by molecules of specific gases along the line of sight. Active remote sensors include the COSPEC, when aimed at an artificial light, and the laser radar (LIDAR) which measures reflections of its own signals from aerosols and particles. These are operational systems. Still others (e.g.,gas filter correlation instruments) are in the developmental stage.

Remote sensors can be used from a fixed point to monitor stack emissions at the exit or to map the pollutant dispersal pattern downwind. If viewing the stack exit, a tripod-mounted remote sensor is panned horizontally across the stem of the plume. This can yield the true gas concentrations, provided the stack diameter and gas exit temperatures are known. Further downwind the stationary remote sensor can measure in a vertical plane through the near-horizontal plume. This can yield the effective stack height and vertical mixing coefficient of the plume for modeling purposes. From one site a number of separate profiles may be obtained for increasing distances downwind simply by changing the horizontal angle between vertical profiles. If the wind speed is known, the net flow of gas across the plane may also be calculated.

Finally, remote sensors can be installed in moving laboratories, along with ground level monitors, to view upward while traversing.

This is the most efficient use of these instruments. This technique permits the integrated measurement of burden of gas overhead and hence the mapping in horizontal coordinates of the vertically integrated total burden of contaminant in the atmosphere. A remote sensor, when operated in a moving laboratory together with ground level monitors, is a powerful device for quantifying the contribution of individual sources to the total air contaminant impact of an airshed.

EXPERIMENTAL DESIGN

Dynamic measurements are especially suited to the study of complicated air monitoring problems, including multiple source pollutants and plume dispersal in rough terrain.

Consider the source and plume illustrated in Figure 1. The contaminant is emitted from the source into the atmosphere and dispersed. The dispersal is controlled by the wind speed and atmospheric stability. The ground level concentrations downwind depend on the amount of contaminant emitted, the atmospheric dispersal parameters and position. However, the contaminant may be emitted into an atmosphere already bearing some other source's effluent. The air flow may be distorted by hills near the plant.

The moving laboratory with its remote sensor and point monitors is able to separate the contaminant plume from other such plumes which may be in the area. By traversing upwind as well as downwind, it establishes the background into which the gas is dispersed. It can then map the downwind dispersal patterns to locate the point of maximum ground level concentration and to measure the horizontal crosswind dimension of the plume.

A remote sensor can be set up at the site to make lateral observations of the plume from the site. It first is scanned upwind to define background conditions. Then it is used to measure the vertical profile of the plume to determine its vertical dimension and the effective stack height.

Simultaneously, dynamic meteorological measurements can be made to determine the character of the dispersing atmosphere. Double theodolite tracking of pilot balloons permits the accurate measurement of the vertical wind profile and hence the wind speed at the elevation of the plume. The vertical temperature profile is obtained either from a sensor attached to the balloon or with a light aircraft. Data from a met tower provides continuous surface conditions with which to correlate the upper atmospheric data.

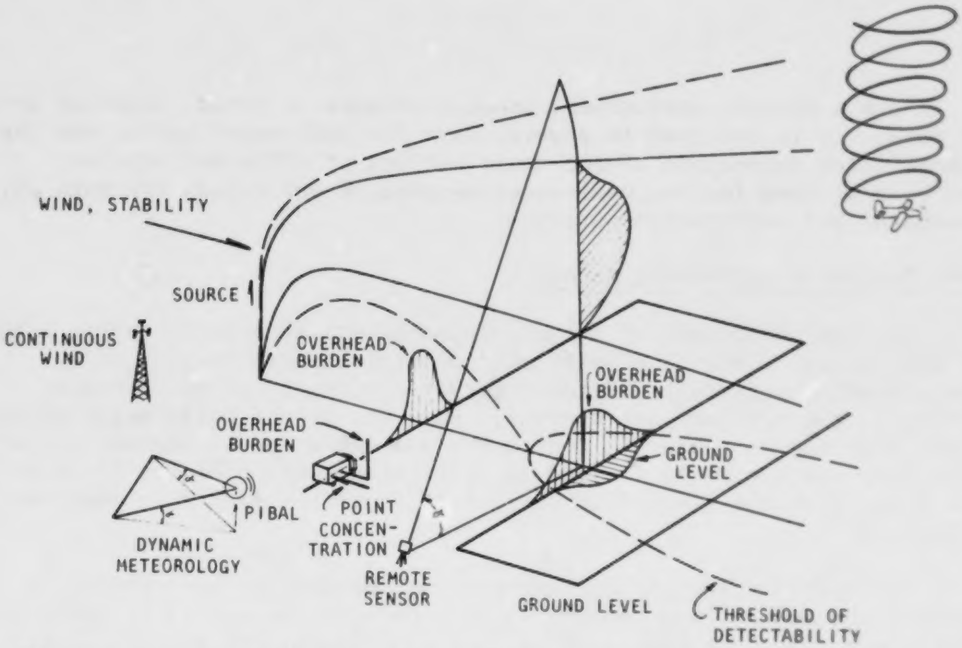
WIND, STABILITY
SOURCE
CONTINUOUS WIND
OVERHEAD BURDEN
OVERHEAD BURDEN
OVERHEAD BURDEN
GROUND LEVEL
PIBAL
DYNAMIC METEOROLOGY
POINT CONCENTRATION
REMOTE SENSOR
GROUND LEVEL
THRESHOLD OF DETECTABILITY

Figure 1. Complete plume characterization by dynamic measurements

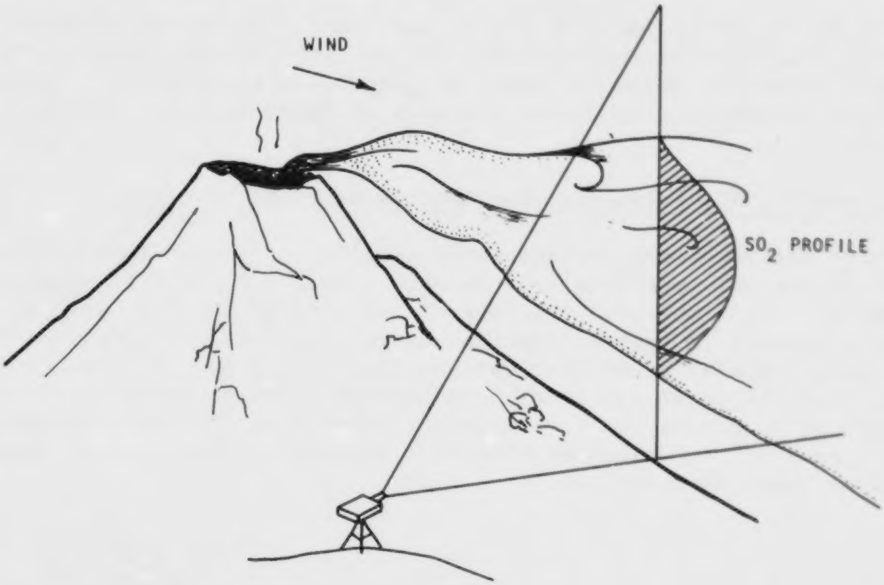
WIND
SO_2 PROFILE

Figure 2. Sketch showing configuration of volcanic emissions and remote sensor. Rate of SO_2 emission was calculated by multiplying the wind velocity by the measured SO_2 load in the plume

Such a dynamic measurement program produces a broad, detailed array of data. It is designed to provide data for both model tuning and the quantitative separation of the contributions of different sources. It can also be used for reconnaissance mapping of gas clouds for both environmental and exploration purposes.

APPLICATION IN GEOTHERMAL AREAS

The limited access of a typical geothermal area in the early stages of development places a significant constraint on the design of a measurement experiment. If the observations are to be made from an aircraft, the problems are minimal. However, ground based measurements with point monitors are limited to the available roads. Remote sensor locations are similarly limited to sites within reach of the field team. The ability of the field team becomes an important factor in measurement planning.

The specific targets of interest must be defined beforehand. Whether the source is a venting well, a natural geyser, or an operating power unit, its location relative to roads, topography and the dispersing wind, and the possibility of cyclical emissions will, of course, control what is measured and where.

In the early stages of a field experiment dynamic measurements can also serve as a reconnaissance tool to identify possible sources of airborne molecules whose presence was previously unsuspected. Those targets are usually natural sources such as fault zones or old mine workings.

Example: SO_2 Emissions from Central American Volcanoes

Near active volcanoes, access is usually so limited that a remote sensor is the only practical way to obtain data. A study by Stoiber and Jepsen (1973) measured the rate of emission of SO_2 from several active volcanoes in Central America, using a correlation spectrometer and dispersing wind speed observations (see Figure 2). This study concluded that the total emissions from Central American volcanoes were at the rate of 1300 tons per day. Table 1 identifies the measured emission rate of each of the volcanoes studied. No other technology was capable of making these observations.

TABLE 1

AMOUNTS OF SO_2 GAS ISSUING FROM VOLCANOES IN GUATEMALA, EL SALVADOR, AND NICARAGUA.

Volcano	SO_2 (metric tons per day)
Guatemala	
Santiaguito	420
Fuego	40*
Pacaya	260
Nicaragua	
San Cristobal	360
Telica	20*
Momotombo	50*
Masaya	180
TOTAL	1330†

*Data less reliable. †Very small plumes issued from fumaroles in the craters of the volcanoes Santa Ana and Izalco, El Salvador. Very approximate estimates from field data suggest that these plumes account for no more than a few tons of SO_2 per day.

(Reproduced from Stoiber and Jepsen, 1973)

Example: Mercury at The Geysers, California

In a program carried out in 1971 to map metallic mercury vapor levels near areas of natural and man-made mercury concentration (Jepsen, 1973), dynamic ground level observations were made at a number of locations, including The Geysers area of Northern California.

The measurement system included a fast response metallic mercury vapor detector and strip chart recorder mounted in a generator-equipped vehicle. The sensor was an atomic absorption spectrophotometer sensitive to $5 \times 10^{-9} gm/m^3$ with a time response of a few seconds. The instrument was a continuous monitor originally developed by Barringer Research Ltd. for prospecting and was rugged enough to withstand the rigors of our field work. Calibration was carried out periodically in the field by injecting an aliquot of mercury into the sample line. The system was also zeroed periodically in the field by passing the sample air flow through a mercury scrubber (>96% efficiency) upstream from the analysis chamber. Figure 3 illustrates the complete measurement system.

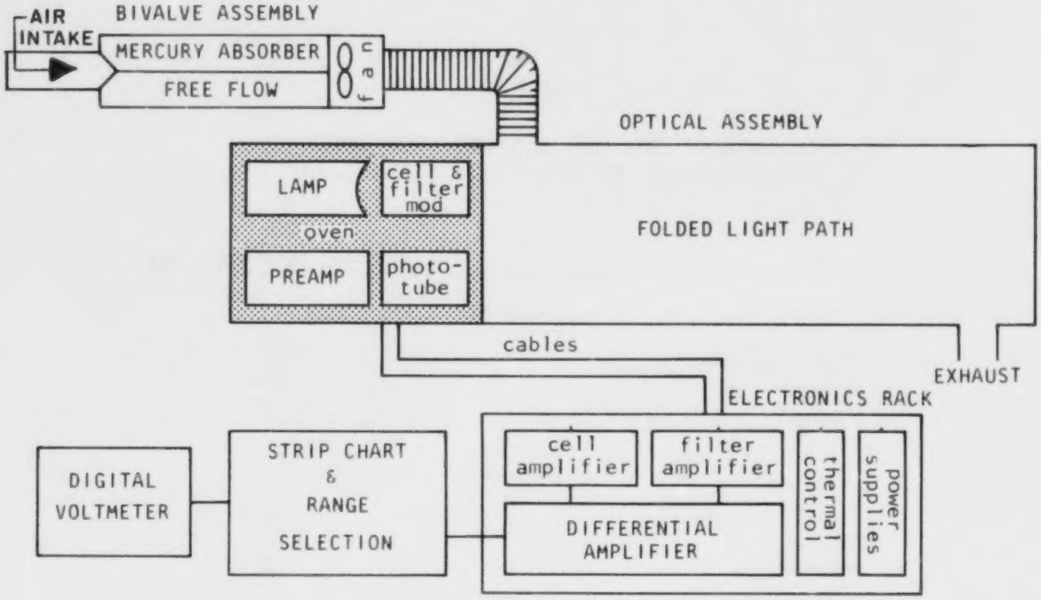
AIR INTAKE
BIVALVE ASSEMBLY
MERCURY ABSORBER
FREE FLOW
fan
OPTICAL ASSEMBLY
LAMP
cell & filter mod
oven
PREAMP
photo-tube
FOLDED LIGHT PATH
cables
EXHAUST
ELECTRONICS RACK
DIGITAL VOLTMETER
STRIP CHART & RANGE SELECTION
cell amplifier
filter amplifier
DIFFERENTIAL AMPLIFIER
thermal control
power supplies

Figure 3. Simplified block diagram of mercury vapor measurement system.

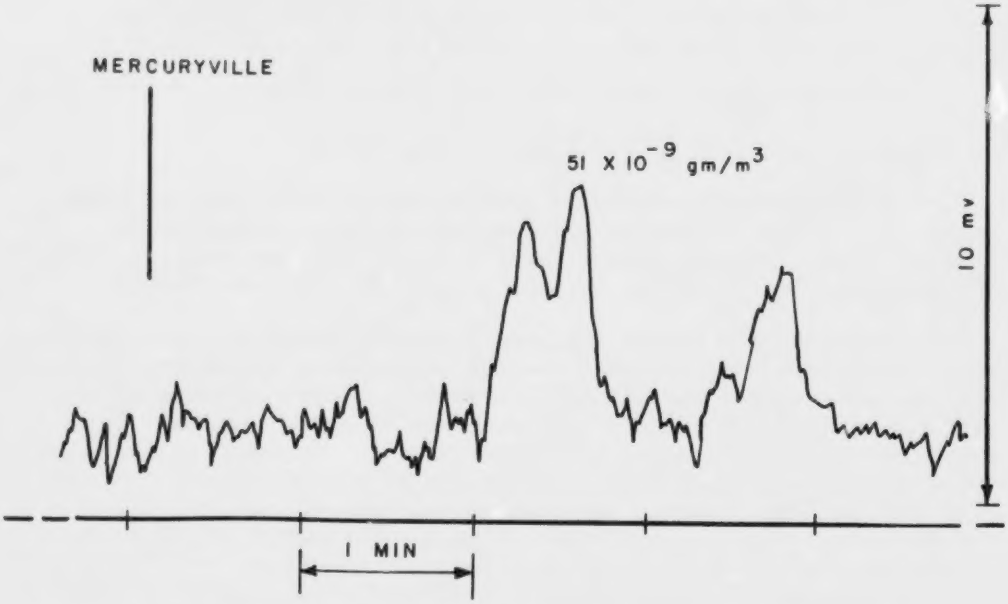

Figure 4. Portion of strip chart record showing mercury background and low peak.

The data obtained on February 15, 1971 show the character of data possible from such a survey. The measurement system was operated throughout a traverse from Geyserville northward into The Geysers Resort. Figure 4 shows the nature of the signal as recorded at a high sensitivity setting on the strip chart. Key locations were noted on the strip chart to facilitate later correlation of the data with position. Whenever signals greater than the dynamic range of the recorder were anticipated, the recorder scale was reduced to permit accurate measurement of the peak values. (Today on-board microcomputers and inertial guidance systems do all the work of spatial correlation and scale adjustment, and even draw maps and profiles in real time as the traverse is carried out.)

The presence of apparently naturally occurring mercury vapor in the atmosphere was detected at two separate areas along the traverse (Figure 5). The first was about 800 meters northeast of Mercuryville where a peak of 51×10^{-9} gm/m^3 was observed. The second area contained four peaks, located along the road beside Big Sulfur Creek from Adit #2 of Buckman Mines (300×10^{-9}gm/m^3) eastward to the power plant at The Geysers (900×10^{-9}gm/m^3). Along the way a peak of about 800×10^{-9} gm/m^3 was observed near The Geysers Resort.

Past the power plant the traverse led up the side of the hill between venting wells. Levels there ranged from 3500×10^{-9} gm/m^3 along the road to a single observation of $28{,}000 \times 10^{-9}$gm/m^3 taken while directly sampling a venting well.

The meteorology was probably very important in controlling the levels observed that day. Winds were light from the west, tending to move the gaseous material gently eastward from its source. As a result there may have been a general funneling and recirculation of the air in the valley, explaining the high ambient levels measured at The Geysers and the Resort.

The data near Mercuryville, however, is less easy to explain, since the mine development is some distance from the road. There is some topography which might interfere with atmospheric dispersion. However, another explanation is possible.

A geological map of the area shows a zone of alteration, reflecting a permeable fracture zone, crossing right at the location of the peak (Erskine, 1977). This coincidence of fracture zone and airborne mercury vapor suggests that the mercury may have been naturally emitted from the fracture. If this were the case, then in other areas the presence of mercury vapor may also indicate the location of permeable fracture zones. In particular, the presence of that zone in the Big Sulfur Creek area suggests that the mercury levels there may be due

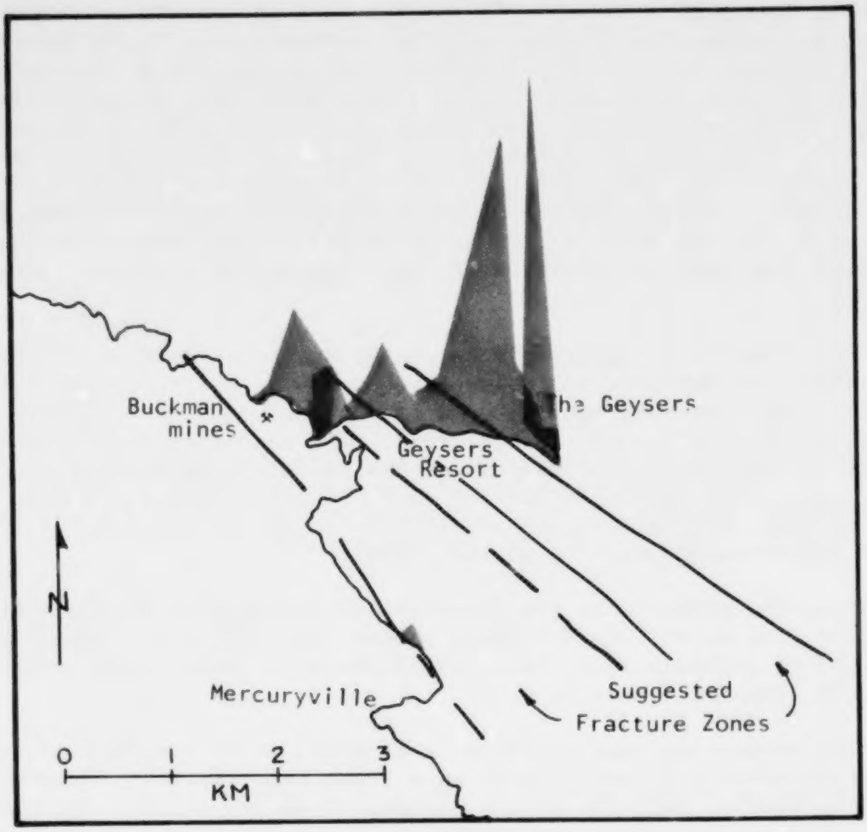
Buckman mines
The Geysers
Geysers Resort
N
Mercuryville
Suggested Fracture Zones
0
1
2
3
KM

Figure 5. Profile showing mercury concentrations measured along traverse route and mapped zones of permeable fracture

not only to human activity in both geothermal development and mercury mining, but also in significant part to emissions from the local geology. Pre-development measurements may have supported this idea.

If the presence of mercury vapor is a reliable guide to zones of fracture and permeability in the local geology, then the dynamic measurement of that gas in the atmosphere could also serve as a tool to map heat conducting zones. In that case, the usefulness of the dynamic measurement of mercury vapor in geothermal areas would have come full circle, back to its original intent of geological exploration.

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ABSTRACT

ANALYSIS OF RADON IN GEOTHERMAL EFFLUENTS

P. Kruger
Stanford University, Stanford, California

Sampling and analysis of geothermal effluents is an important problem in the effort to ensure the development of geothermal energy in an environmentally responsible manner. Yet the need for good sampling and analytical methods is common to many operational aspects of geothermal energy across the full cycle of exploration, assessment, production, and utilization. An example is the study of radon emanation in geothermal fluids. Radon sampling, detection and measurement have had extensive study because radon is a radioactive gas. Yet as a chemical constituent of geothermal fluids it can act as an internal tracer for studies of reservoir physics and engineering. The concentration of radon in produced geofluids depends on several independent factors, among them the distribution of radium in the formation, the emanating power of the produced radon, and the transport time of the radon from emanation to sampling sites.

The distribution of radium in a geothermal system is a function of the hydrochemical and thermochemical history of the formation and its infiltrating geofluids. The emanating power is a function of the physical state of the formation. And the transport time of the radon is a function of the hydrodynamic properties of the reservoir. Thus, studies of radon concentration in produced geofluids, as a function of time in a single well, in wells distributed over a geothermal area, and in wells in different geothermal areas, each with flow conditions as a major parameter, may afford a detailed understanding not only of the role of radon as a component of geothermal fluids, but also of reservoir transport phenomena both under steady-flow and transient-flow conditions.

ABSTRACT

NOBLE GAS SAMPLING OF THE GEOTHERMAL HEAT LOOP AT NILAND FIELD, CALIFORNIA

M. O'Connell
U.S. Environmental Protection Agency
Office of Radiation Programs, Las Vegas, Nevada

This paper will describe the sampling method and present the analytical results of a recently completed study at the San Diego Gas and Electric Geothermal Facility in the Imperial Valley of California. A program to sample Radon-222, Argon, and Helium at the 3 stages of steam-water separation, the geothermal brine supply well and at the non-condensible exhaust stack is described in detail. There was a hope to describe the technology on a mass balance scale but because of uncertain flow conditions, the results were expressed in a correlated manner.

This study was performed by personnel from the U.S. EPA Office of Radiation Programs, Lawrence Livermore Laboratory, and the U.S. Geological Survey.

A REVIEW OF THE DETERMINATION OF HYDROGEN SULFIDE IN AIR BY THE CADMIUM HYDROXIDE-STRACTAN COLORIMETRIC METHOD:

Current Practices and Modifications

R. A. McCurdy and S. L. Altshuler
Pacific Gas and Electric Company
Department of Engineering Research
San Ramon, California

SUMMARY

An in-depth analysis has been performed on several calibration procedures for the cadmium hydroxide-STRactan method for one-hour sampling of ambient hydrogen sulfide (H_2S) concentrations. This is the method recommended by the California Air Resources Board. Results show the calibration procedures to be susceptible to varying sulfide losses during the development of the color depending on the glassware and volumes of reagents used. Agreement can be achieved between the use of aqueous sulfide solutions standardized by an iodometric titration and the use of gravimetrically calibrated H_2S permeation tubes when similar glassware and reagent volumes are used.

In addition, the use of the cadmium hydroxide-STRactan method for 24-hour sampling was evaluated; a 46 percent loss was observed.

INTRODUCTION

The cadmium hydroxide-STRactan method is the referee method for the determination of hourly average ambient H_2S concentrations in the State of California. Recent experience has shown differences of 20 to 30 percent between various calibration procedures for this method. The more recent, popular use of calibrated permeation tubes, whereby the concentration of a calibration gas is determined gravimetrically, has disagreed with the results when the method is calibrated using aqueous sulfide solutions standardized by iodometric titrations. As a result of these discrepancies, considerable effort has been devoted by Department of Engineering Research personnel to investigate the procedures for the preparation of calibration curves in the laboratory and for the samples in the field. The results of these investigations are reported herein.

ANALYTICAL PROCEDURE USING THE CADMIUM HYDROXIDE-STRACTAN METHOD FOR THE MEASUREMENT OF H_2S IN AMBIENT AIR, 100 ppb

The cadmium hydroxide-STRactan method for the determination of H_2S in ambient air has been described by several authors. 1,2,3 The chemical reagents used in the method are all analytical grade, ACS. The accepted procedure is described in Appendix A. Work described herein involved some modifications of this procedure. In working with aqueous calibration procedures, extreme care must be exercised to insure the use of oxygen-free water or some of the dissolved sulfide can be lost by oxidation. This water is prepared by boiling deionized-distilled water to expel dissolved oxygen, and then cooling while bubbling ultrapure nitrogen through the water to prevent oxygen from becoming redissolved.

LABORATORY CALIBRATION OF THE CADMIUM HYDROXIDE-STRACTAN METHOD

Three different procedures to prepare a calibration curve for the cadmium hydroxide-STRactan method have been compared: (1) sodium sulfide, $Na_2S \cdot 9H_2O$, has been used to prepare an aqueous sulfide solution which is then standardized by iodometric titration, (2) pure CP grade H_2S gas has been used to generate a standard aqueous sulfide solution, and (3) a gravimetrically calibrated H_2S permeation tube has been used to generate an H_2S stream of known concentration. In addition, different types of volumetric glassware have been investigated to determine if they could affect the calibration curve.

1. Use of Sodium Sulfide in the Preparation of a Standard Sulfide Solution

The sodium sulfide stock solution was prepared by first washing a crystal of $Na_2S \cdot 9H_2O$, weighing about 1.5 grams, in deionized water while being contained in a beaker. In this manner, most thiosulfates and other polysulfides which may interfere positively in the later iodometric standardization of the sulfide stock solution were eliminated. The crystal was washed down to approximately 0.2 gm in weight and quickly placed in a nitrogen purged 1000-ml volumetric flask. The flask was quickly filled to volume with oxygen-free water and mixed thoroughly. This stock standard contained the equivalent of approximately 28.3 mg H_2S/liter.

Standardization was then performed on the stock solution. 25 ml of standard 0.01N iodine were pipetted into a 250-ml erlenmeyer flask containing 50 ml of deionized water. 10 ml of 50% V/V HCl were then added to the flask. 50 ml of the stock sulfide solution were accurately pipetted into the flask, and the mixture was immediately back-titrated with 0.01N sodium thiosulfate to the starch endpoint. The starch indicator was not added to the flask until the iodine had turned to a pale yellow color. The entire titration was done in less than two minutes. A blank determination using 25 ml of iodine was run prior to the back-titration. Duplicate runs were made which were within 5 ppt* in precision. Immediately after the titration was completed, 50 ml of the stock sulfide solution were pipetted into a clean nitrogen purged 100-ml volumetric flask. The flask was filled to volume with oxygen-free water and mixed thoroughly. This working solution contained approximately 14.2 $\frac{\mu gm}{ml}$ H_2S equivalent to 10.2 $\frac{\mu l}{ml}$ H_2S at 25°C, 1 atm. The individual standards for establishing the calibration curves were prepared using 100-ml volumetric flasks. 0, 1, 2, 3, 4, 5, 6, 7 ml of working solution were quickly pipetted into each of seven volumetrics containing about 25 ml of the cadmium hydroxide absorbing solution. An Epindorff pipette was used to expedite pipetting. The standards were then filled to the 100-ml mark with additional absorbing solution, and mixed thoroughly. This corresponded to standards with 0, 1, 2, 3, 4, 5, 6, 7 µl H_2S for each 10 ml of absorbing solution. 3.0 ml of amine solution were then added to each flask without mixing, followed immediately (within 10 seconds) by 2.0 ml ferric chloride solution. The seven standards were then stoppered and mixed thoroughly to develop the methylene blue color. Each standard was developed for color one at a time. Twenty minutes were allowed for complete color development. Each standard was then read on a spectrophotometer in the visible range at 670 nm using the blank standard to zero the instrument, and a calibration curve was drawn (Curve 1, Figure 1). Curve 1 represents a statistical average using a least squares analysis of nine calibrations. This curve is described best by the equation:

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*parts per thousand

$$\frac{\mu l}{10\ ml} = 4.29\ (ABS)^2 + 5.6\ (ABS) + 0.059$$

where:

ABS is the color absorbance as read on a spectrophotometer

$\frac{\mu l}{10\ ml}$ are the µl of H_2S in 10 ml of absorbing solution at 25°C, 1 atm.

To evaluate if oxidizable compounds other than H_2S were present in the sodium sulfide crystals, stock solutions were also prepared by withdrawing 20 cc of CP grade H_2S gas from a lecture bottle fitted with a pressure regulator, and injecting it through a rubber septum placed on the top of a 1-liter volumetric flask containing 0.01M sodium hydroxide made with distilled deionized water. The flask was inverted so the H_2S gas bubbled through the solution. The solution was then mixed thoroughly and standardized using the same procedure as for the solid sodium sulfide standard, and a calibration curve was prepared. This curve was essentially the same as Curve 1, Figure 1.

2. Use of a Gravimetrically Calibrated H_2S Permeation Tube

A permeation tube with an emission rate of 1 µg/min of H_2S established previously by accurate weighings, was stabilized at a constant temperature of 30°C in a permeation oven. Nitrogen was used as the carrier gas over the permeation tube. The total flow out of the permeation oven was adjusted to one liter per minute. A midget impinger containing 10 ml of cadmium hydroxide-STRactan absorbing solution was connected to the total output of the permeation oven. The oven output was sampled for seven different, known periods to time in order to collect

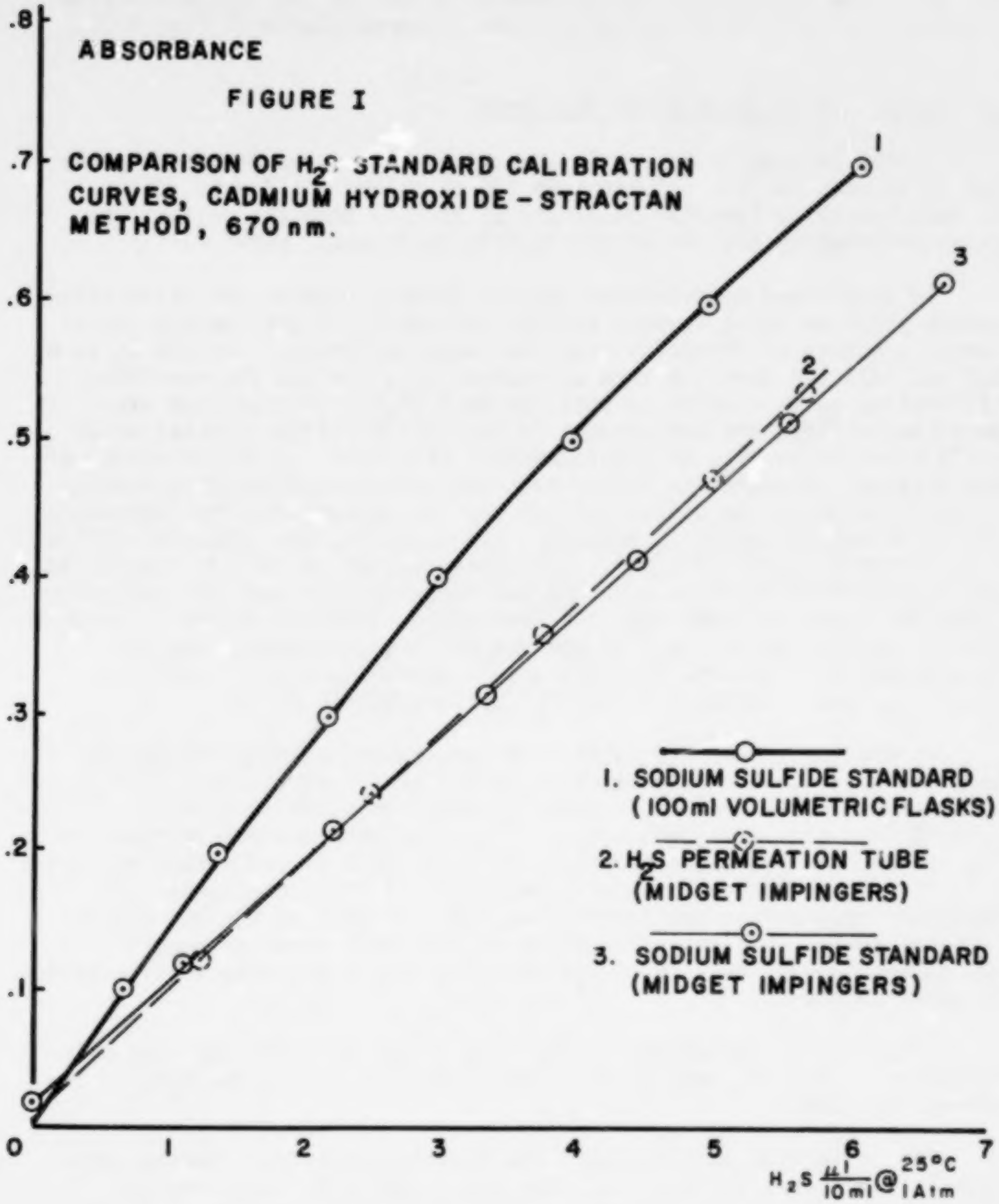

Figure 1. Comparison of H_2S standard calibration curves. Cadmium hydroxide-STRactan method, 670 nm

standards with the equivalent of 1-7 µl H_2S per 10 ml of absorbing solution. The methylene blue color was developed in the impingers by adding 0.3 ml of the amine solution followed by 0.2 ml of the ferric chloride solution. A calibration curve was then prepared (Curve 2, Figure 1).

3. Comparison of Calibration Standards

As can be seen in Figure 1, the calibration curve prepared by the use of aqueous sulfide solutions in 100 ml volumetric flasks, Curve 1, is more sensitive (greater color per µl of H_2S) than the calibration curve prepared by the use of gravimetric techniques, Curve 2.

In an attempt to determine the discrepancy between the calibration curves prepared using aqueous sulfide solutions and gravimetric procedures, a number of investigations have been performed. The use of pure H_2S gas injected directly into an aqueous solution and the resulting calibration curve similar to that for $Na_2S \cdot 9H_2O$ indicated that other possible sulfides are not present in the sodium sulfide crystal which could bias the results of the iodometric titration. A determination of the sulfide concentration in the standardized aqueous solution made by actually weighing the sodium sulfide crystal agreed with the iodometric titration results within 2 percent. Consequently, the iodometric titration is not a source of error. The concentration of sulfide present in the aqueous solution when pure H_2S was injected into solution was calculated and found to agree with the iodometric titration within 10 percent. This 10 percent still does not account for the discrepancy and can largely be attributed to possible volume-measuring errors occurring during the gas transfer from the H_2S lecture bottle to the flask.

An examination of the calibration procedures using a permeation tube indicated that the gravimetric determination of the rate of H_2S emission could be in error if other non-H_2S compounds were being emitted from the permeation tube. Discussion with the manufacturer of the permeation tube indicated that the tubes were filled with high purity H_2S. In an attempt to physically determine if other compounds were being emitted, a mass spectrometer was used to analyze the gas emitted from the tube. This analysis, while at its lower range of sensitivity due to the tube's low rate of H_2S emission, did not indicate the presence of other compounds.

Error due to variations in the rate of H_2S emission was also eliminated as it did not vary by more than 2 percent during the life of the permeation tube.

The collection efficiency of the cadmium hydroxide-STRactan solution in the midget impinger was also investigated by analyzing the reagent of a second impinger placed in series while sampling a stream of H_2S. No significant H_2S was recovered in the second impinger indicating complete recovery of H_2S in the initial impinger.

The effect of temperatures on color development had been previously studied in an effort to achieve agreement between the two methods of calibration. Calibration curves were prepared using 100 ml volumetric flasks and midget impingers immersed in a 0°C ice bath. All reagents used were also kept at 0°C. The resulting calibration curves still remained about 20-30 percent apart in value, but both were higher in sensitivity. As before, the decreased temperature caused the methylene blue color to be more intense than at ambient conditions.

Further analysis of the different calibration methods indicates that a loss of H_2S could be occurring during the color-developing procedures. When the acidic amine solution is added to cadmium hydroxide-STRactan reagent that contains H_2S, H_2S gas is formed and can escape the solution until the ferric chloride reagent is added. The aqueous sulfide method of calibration uses 100 ml of reagent of high sulfide content (by sheer volume alone) in a volumetric flask where the total air-exposed surface area to total volume ratio was very small. The gravimetric calibration used 10 ml of reagent in an impinger where the air-exposed surface area to total volume was not nearly as small. Therefore, an investigation was performed to determine the effect of developing the same cadmium hydroxide-STRactan solution (containing sulfide) in different glassware of widely different surface area to total volume ratios.

Curve 3 in Figure 1 shows a calibration curve prepared using aqueous sodium sulfide solution in a midget impinger; good agreement was achieved with the permeation tube calibration, Curve 2. Thus, both the aqueous sodium sulfide solution and gravimetrically calibrated permeation tube procedures can produce the same calibration curves when the same glassware is used, when the final color is developed. This comparison of the two different methods for calibration of the cadmium hydroxide-STRactan method indicates that similar glassware and volumes of reagent must be used when calibrating and sampling. Under these conditions gravimetric calibration using permeation tubes can agree with chemical calibrations based on iodometric titrations, giving equivalent calibration curves (Figure 1, Curves 2 and 3).

As a final check, a total sulfur analyzer with a flame photometric detector (FPD) was used to confirm the emission rate of an H_2S permeation tube. The analyzer was calibrated with sulfur dioxide (SO_2). As SO_2 and H_2S both respond similarly on an FPD detector, this procedure offered an independent check on the determination of the emission rate of the H_2S permeation tube. The emission rate of the H_2S permeation tube measured on the FPD analyzer was 0.127 μg/min. The emission rate determined wet chemically using the gravimetrically prepared calibration curve was 0.130 μg/min; the emission rate was 0.125 μg/min using the calibration curve prepared from the addition of sodium sulfide to impingers. These results further substantiate the modified standardization procedures as being close to absolute.

SAMPLING FOR AMBIENT H_2S CONCENTRATIONS IN THE FIELD

1. 30-Minute Sampling

Ambient H_2S concentrations have been measured monthly at The Geysers since 1971.[5,6] The cadmium hydroxide-STRactan method has been used for sampling; it has been modified based on experience from time to time.[5] Nominally, 30-minute samples are taken at each location using a sampling train as shown in Figure 2. Sample flow is maintained at 2 liters per minute; 10 ml of absorbing solution are used. The effect of sample flow rate on the amount of H_2S collected has been studied. No significant differences in color absorbances were observed when a series of samples were taken from a permeation tube outlet of 0.5, one and two liters per minute for ten-minute periods. The samples are kept in the dark at all times to prevent photodecomposition even during sampling (aluminum foil is wrapped around the impingers to keep the absorbing solution in the dark); and the methylene blue color is developed immediately after taking a sample instead of returning samples to the laboratory for subsequent analysis. The color is read within 24 hours of sampling. Tests have shown that the methylene blue color is very stable up to at least 48 hours if kept at room temperature and in the dark.[5]

The midget impingers are modified to prevent foaming and carry-over of cadmium hydroxide-STRactan solution by increasing the length of the impinger by 75 mm over that of the standard midget impinger and by slipping two Teflon demister discs over the impinger air inlet tube, about 1-2 inches from the top. Ethanol could also be added to reduce foaming, but greater evaporation of reagent would occur. Color losses were observed 74 hours after initial color development when ethanol is used.

2. Twenty-four Hour Sampling

Since it was desired to simultaneously measure 24-hour average ambient H_2S and SO_2 concentrations at The Geysers, investigations were made to determine recovery of H_2S during 24-hour sampling. The sampling train (Figure 3) was exactly the same as that for the pararosaniline procedure employed by the EPA as their Standard Reference Method for SO_2.[7] Polypropylene bubblers containing the cadmium hydroxide-STRactan absorbing solution were used instead of the standard glass impingers. Flow control was accomplished by critical flow orifices which were 27-gauge hypodermic needles. This size gives a nominal 0.2 liter per minute flow. Constant H_2S concentrations of 18, 23, and 40 ppb in air were provided to the sampling train.

The results obtained, shown in Table 1, were calculated using the calibration curve prepared with 100-ml volumetric flasks, Figure 1, Curve 1. The permeation rate from the H_2S tube was calibrated against

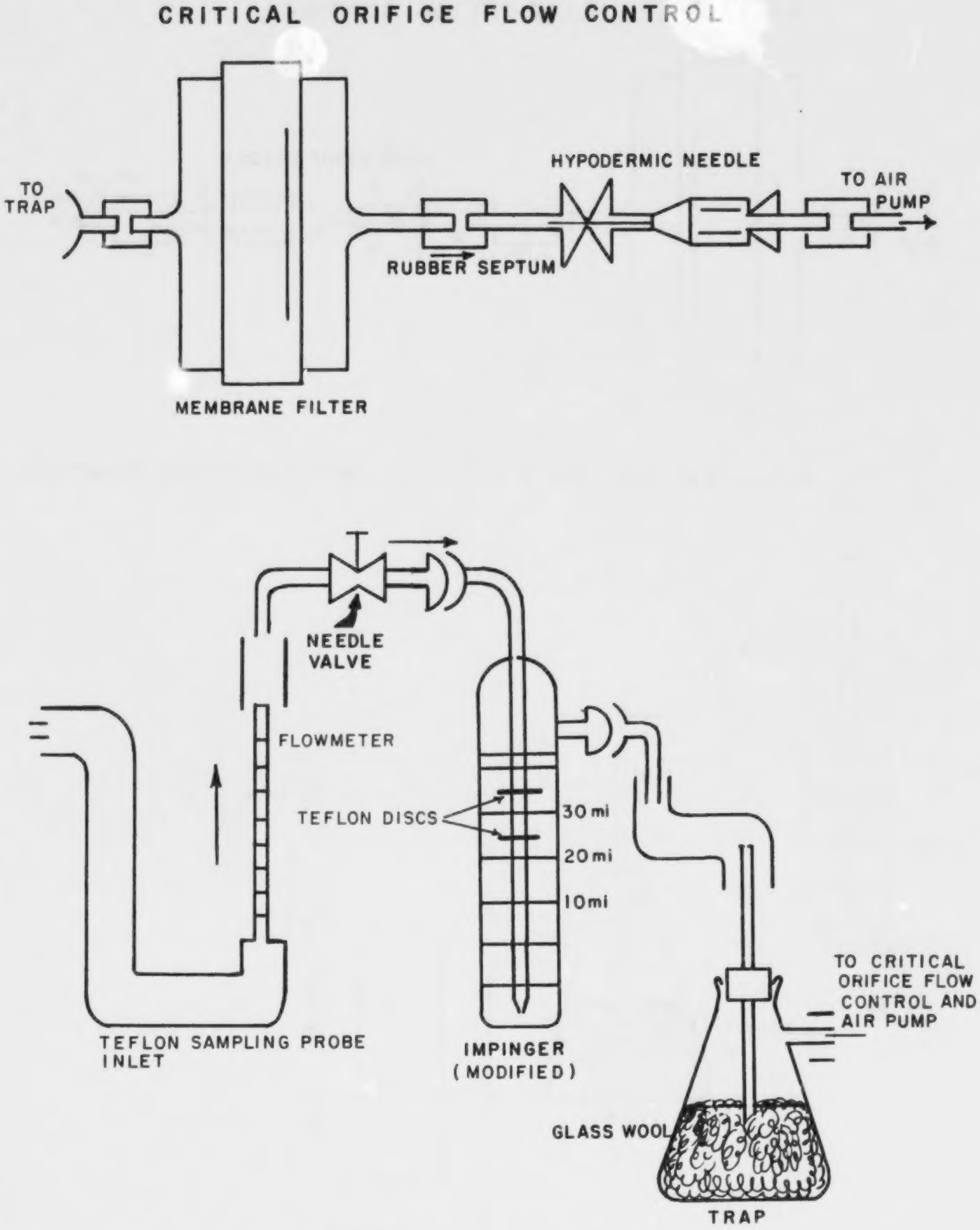
CRITICAL ORIFICE FLOW CONTROL
TO TRAP
HYPODERMIC NEEDLE
TO AIR PUMP
RUBBER SEPTUM
MEMBRANE FILTER
NEEDLE VALVE
FLOWMETER
TEFLON DISCS
30 mi
20 mi
10 mi
TEFLON SAMPLING PROBE INLET
IMPINGER (MODIFIED)
TO CRITICAL ORIFICE FLOW CONTROL AND AIR PUMP
GLASS WOOL
TRAP

Figure 2. 30 minute sampling train.

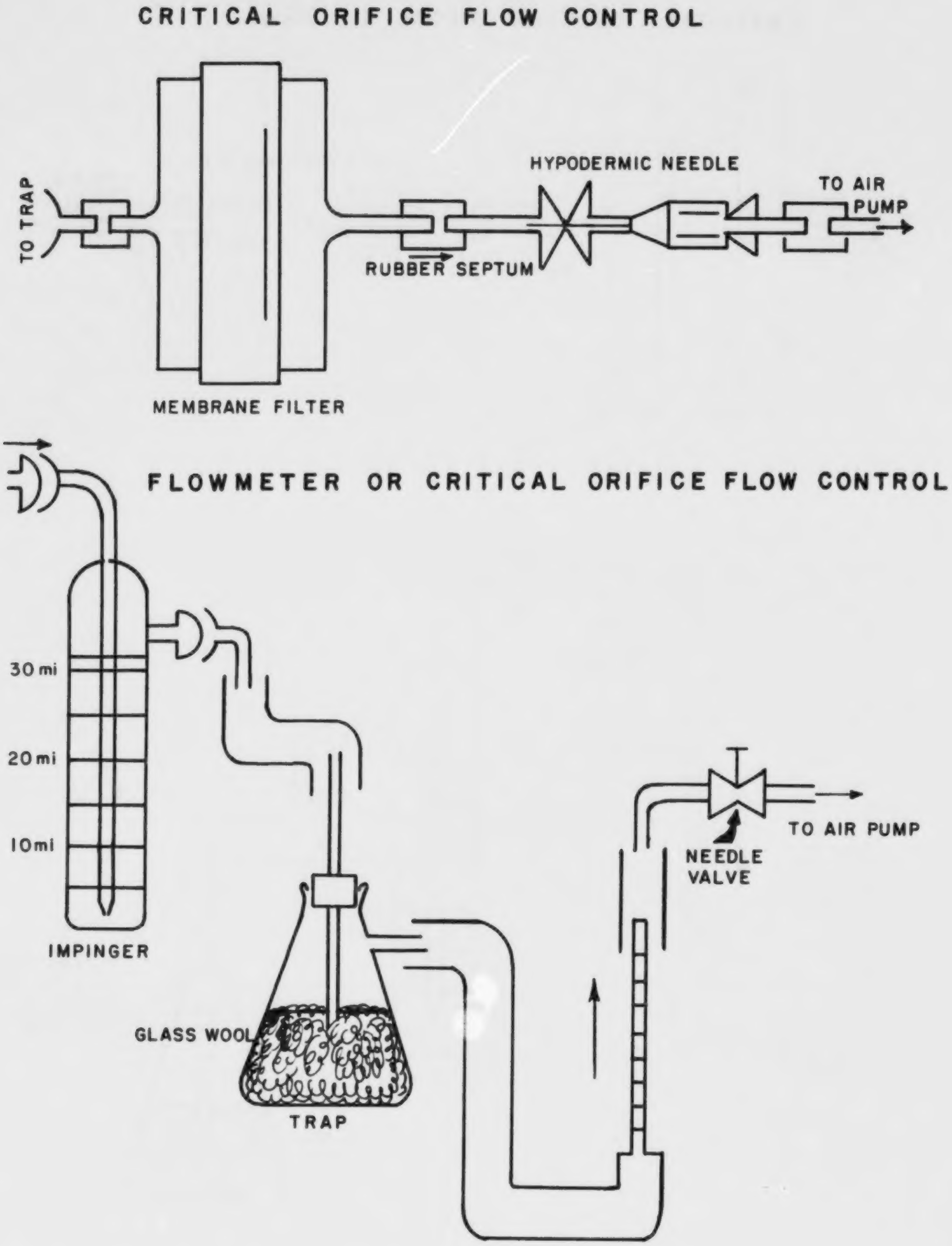
CRITICAL ORIFICE FLOW CONTROL
TO TRAP
MEMBRANE FILTER
RUBBER SEPTUM
HYPODERMIC NEEDLE
TO AIR PUMP
FLOWMETER OR CRITICAL ORIFICE FLOW CONTROL
30 ml
20 ml
10 ml
IMPINGER
GLASS WOOL
TRAP
NEEDLE VALVE
TO AIR PUMP

Figure 3. 24 hour sampling train

Table 1

24-Hour H_2S Sample Recovery

Date	Permeation Effluent Concentration, ppm H_2S	H_2S Concentration as Found, ppm (No. of measurements)
3/9/76	40	22 (5)
3/24/76	40	23 (8)
3/26/76	40	22 (7)
3/29/76	40	26 (8)
4/29/76	23	11 (7)
4/30/76	23	12 (8)
5/1/76	23	13 (8)
5/3/76	23	14 (8)
5/4/76	18	13 (8)
5/8/76	18	11 (8)
5/7/76	18	10 (8)

the same curve so that anomalies resulting from the use of different calibration curves were cancelled out. A statistical analysis using a least squares analysis of the data resulted in the line shown in Figure 4 having a slope of 0.544. This means that using the method described for 24-hour sampling results in about a 46 percent loss of H_2S.

Although there is a significant loss of H_2S during 24-hour sampling, the loss seems to be linear with concentration over the range of 18 to 40 ppb. This loss cannot be immediately explained.

CONCLUSIONS

Analysis of procedures used to prepare calibration curves for the cadmium hydroxide-STRactan method indicates that agreement can be achieved between the use of aqueous sulfide solutions prepared from sodium sulfide and the use of H_2S permeation tubes calibrated gravimetrically if the same glassware and reagent volumes are used. The use of 100 ml volumetric flasks during calibration results in less sulfide loss after the addition of the amine reagent than in the midget impingers used for field testing.

Analysis of the use of the cadmium hydroxide-STRactan method for 24-hour sampling indicates that 54 percent of the input H_2S is recovered from a constant concentration gas stream. This recovery is linear over the range of 18 to 40 ppb.

RECOMMENDATIONS

Results have shown that a gravimetrically calibrated permeation tube emitting 1.0 μg/min H_2S can be used to calibrate the cadmium hydroxide-STRactan method. Use of a permeation tube will more accurately simulate actual field sampling techniques and will best account for losses occurring during color development procedures. Similar procedures are also used for primary calibration of the method for the determination of SO_2. It is therefore recommended that the cadmium hydroxide-STRactan method be calibrated using a gravimetrically calibrated permeation tube emitting approximately 1.0 μg/min. Other tubes emitting at lower rates and of different design are more difficult to calibrate and are not recommended without further investigation.

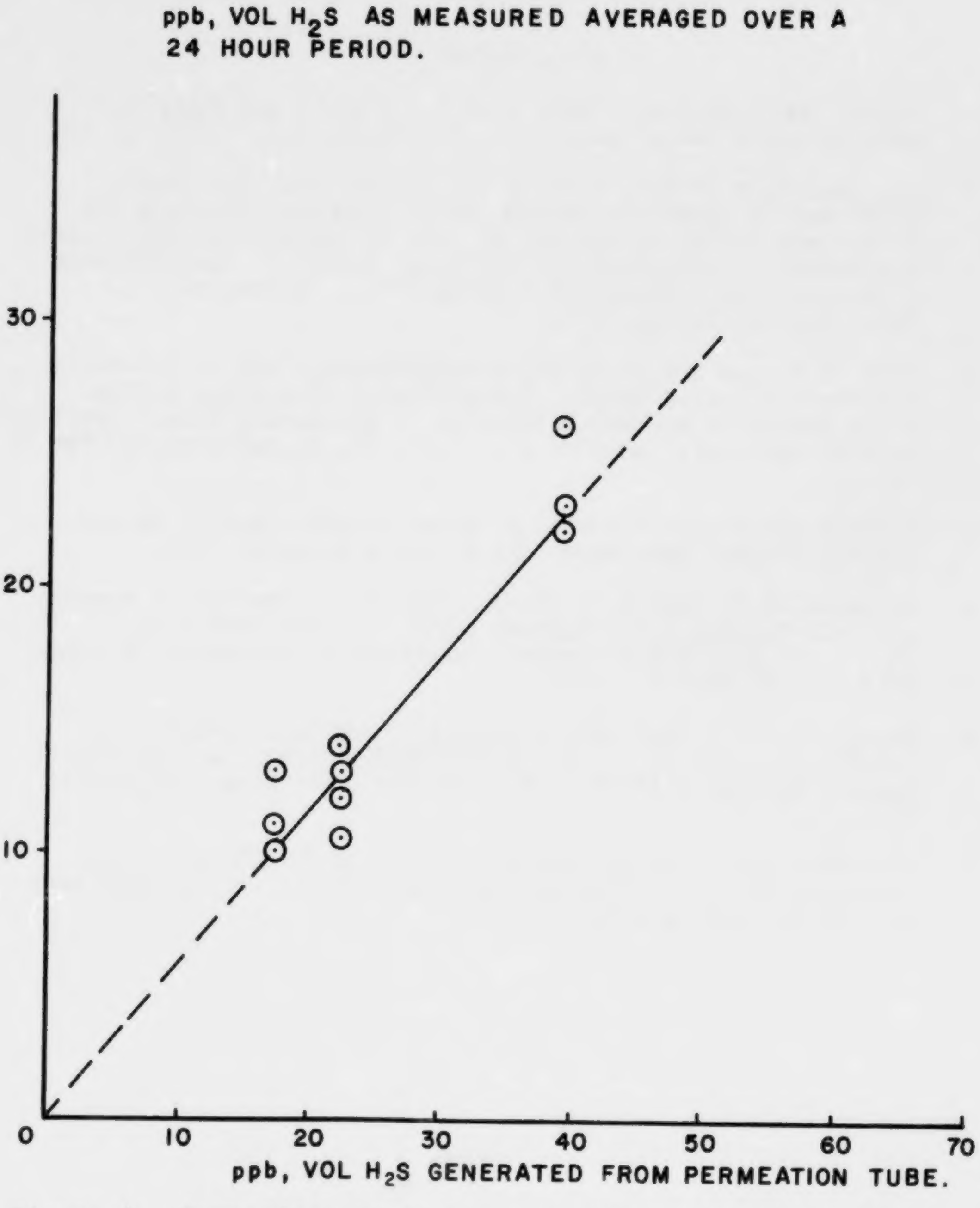

Figure 4. Comparison of 24-hour sampling using the cadmium hydroxide-STRactan method (2 lpm) and concentrations generated from a permeation tube, 0.215 µg/min H_2S

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APPENDIX A. THE DETERMINATION OF HYDROGEN SULFIDE IN AIR BY THE CADMIUM HYDROXIDE-STRACTAN METHOD

HYDROGEN SULFIDE IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Hydrogen Sulfide	Method No.:	P&CAM 126
Matrix:	Air	Range:	0.008 ppm – 50 ppm
Procedure:	Absorption – Methylene Blue – Spectrophotometric	Precision:	Unknown
		Classification:	C (Tentative)
Date Issued:	6/9/72		
Date Revised:	1/15/74		

1. Principle of the Method

1.1 Hydrogen sulfide is collected by aspirating a measured volume of air through an alkaline suspension of cadmium hydroxide (Reference 11.1). The sulfide is precipitated as cadmium sulfide to prevent air oxidation of the sulfide which occurs rapidly in an aqueous alkaline solution. STRactan 10® is added to the cadmium hydroxide slurry to minimize photo-decomposition of the precipitated cadmium sulfide (Reference 11.2). The collected sulfide is subsequently determined by spectrophotometric measurement of the methylene blue produced by the reaction of the sulfide with a strongly acid solution of N, N-dimethyl-p-phenylenediamine and ferric chloride (References 11.3, 11.4, 11.5). The analysis should be completed within 24-26 hours following collection of the sample.

1.2 Hydrogen sulfide may be present in the open atmosphere at concentrations of a few ppb or less. The reported odor detection threshold is in the 0.7-8.4 $\mu g/m^3$ (0.5-6.0 ppb) range (References 11.6, 11.7). Concentrations in excess of 140 $\mu g/m^3$ (100 ppb) are seldom encountered in the atmosphere.

1.3 Collection efficiency is variable below 10 $\mu g/m^3$ and is affected by the type of scrubber, the size of the gas bubbles and the contact time with the absorbing solution and the concentration of H_2S (References 11.8, 11.9, 11.10).

2. Range and Sensitivity

2.1 This method is intended to provide a measure of hydrogen sulfide in the range of 1.1-100 mg/m^3. For concentrations above 70 mg/m^3 the sampling period can be reduced or the liquid volume increased either before or after aspirating. (This method is also useful for the mg/m^3 range of source emissions. For example, 100 mℓ cadmium $(OH)_2$- STRactan 10® media in Greenberg-Smith impingers and 5-minute sampling periods have been used successfully for source sampling.) The minimum detectable amount of sulfide is 0.008 µg/mℓ, which is equivalent to 0.2 µg/m^3 in an air sample of 1 m^3 and using a final liquid volume of 25 mℓ. When sampling air at the maximum recommended rate of 1.5 ℓ/minute for 2 hours, the minimum detectable sulfide concentration is 1.1 µg/m^3 at 760 mm Hg and 25°C.

2.2 Excellent results have been obtained by using this method for air samples having a hydrogen sulfide content in the range 5-50 ppm.

3. Interferences

3.1 The methylene blue reaction is highly specific for sulfide at the low concentrations usually encountered in ambient air. Strong reducing agents (e.g., SO_2) inhibit color development. Even sulfide solutions containing several micrograms sulfide/mℓ show this effect and must be diluted to eliminate color inhibition. If sulfur dioxide is absorbed to give a sulfite concentration in excess of 10 µg/mℓ, color formation is retarded. Up to 40 µg/mℓ, of this interference, however, can be overcome by adding 2-6 drops (0.5 mℓ/drop) of ferric chloride instead of a single drop for color development, and extending the reaction time to 50 minutes.

3.2 Nitrogen dioxide gives a pale yellow color with the sulfide reagents at 0.5 µg/mℓ or more. No interference is encountered when 0.3 ppm NO_2 is aspirated through a midget impinger containing a slurry of cadmium hydroxide-cadmium sulfide-STRactan 10®. If H_2S and NO_2 are simultaneously aspirated through cadmium hydroxide-STRactan 10® slurry, lower H_2S results are obtained, probably because of gas-phase oxidation of the H_2S prior to precipitation as CdS (Reference 11.10).

3.3 Ozone at 57 ppb reduced the recovery of sulfide previously precipitated as CdS by 15 per cent (Reference 11.10).

3.4 Sulfides in solution are oxidized by oxygen from the atmosphere unless inhibitors such as cadmium and STRactan 10® are present.

3.5 Substitution of other cation precipitants for the cadmium in the absorbent (i.e., zinc, mercury, etc.) will shift or eliminate the absorbance maximum of the solution upon addition of the acid-amine reagent.

3.6 Cadmium sulfide decomposes significantly when exposed to light unless protected by the addition of 1 per cent STRactan® to the absorbing solution prior to sampling (Reference 11.2).

3.7 The choice of impinger used to trap H_2S with the $Cd(OH)_2$ slurry is very important when measuring concentration in the range 5-50 ppm. Impingers or bubblers having fritted-end gas delivery tubes are a problem source if the sulfide in solution is oxidized by oxygen from the atmosphere to free sulfur. The sulfur collects on the fritted-glass membrane and may significantly change the flow rate of the air sample through the system. One way of avoiding this problem is to use a midget impinger with standard, glass-tapered tips.

4. Precision and Accuracy

4.1 A relative standard deviation of 3.5 per cent and a recovery of 80 per cent has been established with hydrogen sulfide permeation tubes (Reference 11.2).

5. Advantages and Disadvantages of the Method

5.1 Effect of Light and Storage – Disadvantage

5.1.1 Hydrogen sulfide is readily volatilized from aqueous solution when the pH is below 7.0. Alkaline, aqueous sulfide solutions are very unstable because sulfide ion is rapidly oxidized by exposure to the air.

5.1.2 Cadmium sulfide is not appreciably oxidized even when aspirated with pure oxygen in the dark. However, exposure of an impinger containing cadmium sulfide to laboratory or to more intense light sources produces an immediate and variable photo-decomposition. Losses of 50-90 per cent of added sulfide have been routinely reported by a number of laboratories. Even though the addition of STRactan 10® to the absorbing solution controls the photo-decomposition (Reference 11.2), it is necessary to protect the impinger from light at all times. This is achieved by the use of low actinic glass impingers, paint on the exterior of the impingers, or an aluminum foil wrapping.

6. Apparatus

6.1 Sampling Equipment. The sampling unit for the impinger collection method consists of the following components:

6.1.1 A graduated 25-mℓ midget impinger with a standard glass-tapered gas delivery tube containing the absorbing solution or reagent.

6.1.2 A pump suitable for delivering desired flow rates with a minimum capacity of 2 ℓpm through the impinger. The sampling pump is protected from splashover or water condensation by an adsorption tube loosely packed with a plug of glass wool and inserted between the exit arm of the impinger and the pump.

6.1.3 An integrating volume meter such as a dry-gas or wet-test meter. The air meter must be capable of measuring the air flow within ±2 per cent. A wet- or dry-gas meter, with contacts on the 1-feet^3 or 10-l dial to record air volume, or a specially calibrated rotameter, is satisfactory. Instead of these, calibrated hypodermic needles may be used as critical orifices if the pump is capable of maintaining greater than 0.7 atmospheric pressure differential across the needle (Reference 11.11).

6.1.4 Thermometer.

6.1.5 Manometer.

6.1.6 Stopwatch.

6.2 Associated laboratory glassware.

6.3 Colorimeter with red filter or spectrophotometer at 670 nm.

6.4 Matched cells, 1-cm path length.

7. Reagents

All reagents must be ACS analytical reagent quality. Distilled water should conform to the ASTM Standards for Referee Reagent Water.

All reagents should be refrigerated when not in use.

7.1 Amine-sulfuric Acid Stock Solution. Add 50 mℓ concentrated sulfuric acid to 30 mℓ water and cool. Dissolve 12 g of N, N-dimethyl-p-phenylenediamine dihydrochloride (para-aminodimethylaniline) (redistilled if necessary) in the acid. Do not dilute. The stock solution may be stored indefinitely under refrigeration.

7.2 Amine Test Solution. Dilute 25 mℓ of the Stock Solution to 1 liter with 1:1 sulfuric acid.

7.3 Ferric Chloride Solution. Dissolve 100 g of ferric chloride, $FeC\ell_3 \cdot 6H_2O$, in water and dilute to 100 mℓ.

7.4 Ammonium Phosphate Solution. Dissolve 400 g of diammonium phosphate, $(NH_4)_2HPO_4$, in water and dilute to 1 liter.

7.5 STRactan 10®, (Arabinogalactan) Available from Stein-Hall and Company, Inc., 385 Madison Avenue, New York, New York.

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7.6 Absorbing Solution. Dissolve 4.3 g of $3CdSO_4 \cdot 8H_2O$, and 0.3 g sodium hydroxide in separate portions of water. Mix and add 10 g STRactan 10® and dilute to 1 liter. Shake the resultant suspension vigorously before removing each aliquot. The STRactan®-cadmium hydroxide mixture should be freshly prepared. The solution is only stable for 3 to 5 days.

7.7 H_2S Permeation Tube. Prepare or purchase* a triple-walled or thick–walled Teflon® permeation tube (References 11.10, 11.12, 11.13, 11.14, 11.15) which delivers hydrogen sulfide at a maximum rate of approximately 0.1 μg/minute at 25°C. This loss rate will produce a standard atmosphere containing 50 $\mu g/m^3$ (36 ppb H_2S when the tube is swept with a 2 ℓ/minute air flow. Tubes having H_2S permeation rates in the range of 0.004-0.33 μg/minute will produce standard air concentrations in the realistic range of 1-90 $\mu g/m^3$ H_2S with an air flow of 1.5 ℓ/min.

7.7.1 Concentrated, Standard Sulfide Solution

Transfer freshly boiled and cooled 0.1M NaOH to a liter volumetric flask. Flush with purified nitrogen to remove oxygen and adjust to volume. (Commercially available, compressed nitrogen contains trace quantities of oxygen in sufficient concentration to oxidize the small concentrations of sulfide contained in the standard and dilute standard sulfide standards. Trace quantities of oxygen should be removed by passing the stream of tank nitrogen through a Pyrex or quartz tube containing copper turnings heated to 400-450°C.) Immediately stopper the flask with a serum cap. Inject 300 mℓ of H_2S gas through the septum. Shake the flask. Withdraw measured volumes of standard solution with a 10 mℓ hypodermic syringe and fill the resulting void with an equal volume of nitrogen. Standardize with standard iodine and thiosulfate solution in an iodine flask under a nitrogen atmosphere to minimize air oxidation. The approximate concentration of the sulfide solution will be 440 μg sulfide/mℓ of solution. The exact concentration must be determined by iodine-thiosulfate standardization immediately prior to dilution.

For the most accurate results in the iodometric determination of sulfide in aqueous solution, the following general procedure is recommended:

1. Replace the oxygen from the flask by flushing with an inert gas such as carbon dioxide or nitrogen.

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*Available from Metronics, Inc., 3201 Porter Drive, Palo Alto, California 94304, or PolyScience Corp., 909 Pitner Avenue, Evanston, Illinois 60202.

2. Add an excess of standard iodine, acidify, and back titrate with standard thiosulfate and starch indicator (Reference 11.16).

7.7.2 Diluted Standard Sulfide Solution

Dilute 10 mℓ of the concentrated sulfide solution to 1 liter with freshly boiled, distilled water. Protect the boiled water under a nitrogen atmosphere while cooling. Transfer the deoxygenated water to a flask previously purged with nitrogen and immediately stopper the flask. This sulfide solution is unstable. Therefore, prepare this solution immediately prior to use. This test solution will contain approximately 4 μg sulfide/mℓ.

8. Procedure

8.1 Cleaning of Equipment. All glassware should be thoroughly cleaned; the following procedure is recommended:

8.1.1 Wash with a detergent and tap water solution followed by tap water and distilled water rinses.

8.1.2 Soak in 1:1 or concentrated nitric acid for 30 minutes and then follow with tap, distilled, and double distilled water rinses.

8.2 Collection and Shipping of Samples

8.2.1 Pipet 10 mℓ of the absorbing solution (Section 7.6) into the midget impinger. The addition of 5 mℓ of 95 per cent ethanol to the absorbing solution just prior to aspiration controls foaming for 2 hours (induced by the presence of STRactan 10®. In addition, 1 or 2 Teflon demister discs may be slipped up over the impinger air inlet tube to a height approximately 1-2" from the top of the tube.

8.2.2 Connect the impinger (via the absorption tube) to the vacuum pump with a short piece of flexible tubing. The minimum amount of tubing necessary to make the joint between the prefilter and impinger should be used. The air being sampled should not be passed through any other tubing or other equipment before entering the impinger.

8.2.3 Turn on pump to begin sample collection. Care should be taken to measure the flow rate, time and/or volume as accurately as possible. The sample should be taken at a flow rate of 1.5 ℓpm.

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8.2.4 After sampling, the impinger stem can be removed and cleaned. Tap the stem gently against the inside wall of the impinger bottle to recover as much of the sampling solution as possible. Wash the stem with a small amount (1-2 mℓ) of unused absorbing solution and add the wash to the impinger. Then the impinger is sealed with a hard, non-reactive stopper (preferably Teflon). Do not seal with rubber. The stoppers on the impingers should be tightly sealed to prevent leakage during shipping. If it is preferred to ship the impingers with the stems in, the outlets of the stem should be sealed with Parafilm or other non-rubber covers, and the ground glass joints should be sealed (i.e., taped) to secure the top tightly.

8.2.5 Care should be taken to minimize spillage or loss by evaporation at all times. Refrigerate samples if analysis cannot be done within a day.

8.2.6 Whenever possible, hand delivery of the samples is recommended. Otherwise, special impinger shipping cases designed by NIOSH should be used to ship the samples.

8.2.7 A "blank" impinger should be handled as the other samples (fill, seal and transport) except that no air is sampled through this impinger.

8.3 Analysis

8.3.1 Add 1.5 mℓ of the amine-test solution to the midget impinger through the air inlet tube and mix.

8.3.2 Add 1 drop of ferric chloride solution and mix. (*Note:* See Section 3.1 if SO_2 exceeds 10 μg/mℓ in the absorbing media.)

8.3.3 Transfer the solution to a 25 mℓ volumetric flask. Discharge the color due to the ferric ion by adding 1 drop ammonium phosphate solution. If the yellow color is not destroyed by 1 drop ammonium phosphate solution, continue dropwise addition until solution is decolorized. Make up to volume with distilled water and allow to stand for 30 minutes.

8.3.4 Prepare a zero reference solution in the same manner using a 10 mℓ volume of absorbing solution, through which no air has been aspirated.

8.3.5 Measure the absorbance of the color at 670 nm in a spectrophotometer or colorimeter set at 100 per cent transmission against the zero reference.

9. Calibration and Standards

9.1 Aqueous Sulfide

9.1.1 Place 10 mℓ of the absorbing solution in each of a series of 25 mℓ volumetric flasks and add the diluted standard sulfide solution, equivalent to 1, 2, 3, 4, and 5 μg of hydrogen sulfide to the different flasks.

9.1.2 Add 1.5 mℓ of amine-acid test solution to each flask and mix.

9.1.3 Add 1 drop of ferric chloride solution to each flask. Mix, make up to volume and allow to stand for 30 minutes.

9.1.4 Determine the absorbance in a spectrophotometer at 670 nm, against the sulfide-free reference solution.

9.1.5 Prepare a standard curve of absorbance vs. μg H_2S/mℓ.

9.2 Gaseous Sulfide. Commercially available permeation tubes containing liquefied hydrogen sulfide may be used to prepare calibration curves for use at the upper range of atmospheric concentration. Triple-walled tubes, drilled rod and micro bottles which deliver hydrogen sulfide within a minimum range of 0.1-1.2 μg/minute at 25°C have been prepared by Thomas (Reference 11.10); O'Keeffe (References 11.12, 11.13); Scaringelli (References 11.14, 11.15). Preferably the tubes should deliver hydrogen sulfide within a loss rate range of 0.003-0.28 μg/minute to provide realistic concentrations of H_2S (1.5-140 μg/m^3, 1.1-100 ppb) without having to resort to a dilution system to prepare the concentration range required for determining the collection efficiency of midget impingers. Analyses of these known concentrations give calibration curves which simulate all of the operational conditions performed during the sampling and chemical procedure. This calibration curve includes the important correction for collection efficiency at various concentrations of hydrogen sulfide.

9.2.1 Prepare or obtain a Teflon® permeation tube that emits hydrogen sulfide at a rate of 0.1-0.2 μg/minute (0.07-0.14 μℓ/minute at standard conditions of 25°C and 1 atmosphere). A permeation tube with an effective length of 2-3 cm and a wall thickness of 0.318 cm will yield the desired permeation rate if held at a constant temperature of 25°C ± 0.1°C. Permeation tubes containing hydrogen sulfide are calibrated under a stream of dry nitrogen to prevent the precipitation of sulfur in the walls of the tube.

9.2.2 To prepare standard concentrations of hydrogen sulfide, assemble the apparatus consisting of a water-cooled condenser, constant temperature bath maintained at 25°C ±0.1°C cylinders containing pure dry nitrogen and pure dry air with appropriate pressure regulators, needle valves and flow meters for the nitrogen and dry air, diluent-streams. The diluent gases are brought to temperature by passage through a 2-meter-long copper coil immersed in the water bath. Insert a calibrated permeation tube into the central tube of the condenser, maintained at the selected constant temperature by circulating water from the constant-temperature bath, and pass a stream of nitrogen over the tube at a fixed rate of approximately 50 mℓ/minute. Dilute this gas stream to obtain the desired concentration by varying the flow rate of the clean, dry air. This flow rate can normally be varied from 0.2-15 ℓ/minute. The flow rate of the sampling system determines the lower limit for the flow rate of the diluent gases. The flow rate of the nitrogen and the diluent air must be measured to an accuracy of 1-2 per cent. With a tube permeating hydrogen sulfide at a rate of 0.1 μℓ/minute, the range of concentration of hydrogen sulfide will be between 6-400 μg/m³ (4-290 ppb), a generally satisfactory range for ambient air conditions. When higher concentrations are desired, calibrate and use longer permeation tubes.

9.2.3 Procedure for Preparing Simulated Calibration Curves

Obviously one can prepare a multitude of curves by selecting different combinations of sampling rate and sampling time: The following description represents a typical procedure for ambient air sampling of short duration, with a brief mention of a modification for 24 hour sampling.

1. The system is designed to provide an accurate measure of hydrogen sulfide in the 1.4-84 μg/m³ (1-60 ppb) range. It can be easily modified to meet special needs.

2. The dynamic range of the colorimetric procedure fixes the total volume of the sample at 186 ℓ; then, to obtain linearity between the absorbance of the solution and the concentration of hydrogen sulfide in ppm, select a constant sampling time. This fixing of the sampling time is desirable also from a practical standpoint: In this case, select a sampling time of 120 minutes. Then to obtain a 186 ℓ sample of air requires a flow rate of 1.55 ℓ/minute. The concentration of standard H_2S in air is computed as follows:

$$C = \frac{P_r \times M}{(R + r)}$$

where:

C = Concentration of H_2S in ppm
P_r = Permeation rate in μg/minute
M = Reciprocal of vapor density, 0.719 $\mu \ell/\mu g$
R = Flow rate of diluent air, liter/minute
r = Flow rate of diluent nitrogen, liter/minute

3. The data for a typical calibration curve are listed in Table 1.

TABLE 1

TYPICAL CALIBRATION DATA

Concentrations H_2S, ppb	Amount of H_2S in μl/186 liters	Absorbance of Sample
1	.144	.010
5	.795	.056
10	1.44	.102
20	2.88	.205
30	4.32	.307
40	5.76	.410
50	7.95	.512
60	8.64	.615

4. A plot of the concentration of hydrogen sulfide in ppm (x – axis) against absorbance of the final solution (y – axis) will yield a straight line, the reciprocal of the slope of which is the factor for conversion of absorbance to ppm. This factor includes the correction for collection efficiency. Any deviation from the linearity at the lower concentration range indicates a change in collection efficiency of the sampling system. If the range of interest is below the dynamic range of the method the total volume of air collected should be increased to obtain sufficient color within the dynamic range of the colorimetric procedure. Also, once the calibration factor has been established under simulated conditions the conditions can be modified so that the concentration of H_2S is a simple multiple of the absorbance of the colored solution.

5. For long-term sampling of 24-hour duration, the conditions can be fixed to collect 1200 ℓ of sample in a larger volume of STRactan 10®-cadmium hydroxide. For example, for 24 hours at 0.83 ℓ/min, approximately 1200 ℓ of air are scrubbed. An aliquot representing 0.1 of the entire amount of sample is taken for the analysis.

6. The remainder of the analytical procedure is the same as described in the previous paragraph.

9.2.4 The permeation tubes must be stored in a wide-mouth glass bottle containing silica gel and solid sodium hydroxide to remove moisture and hydrogen sulfide. The storage bottle is immersed to two-thirds its depth in a constant temperature water bath in which the water is controlled at 25°C ±0.1°C.

Periodically, (every 2 weeks or less) the permeation tubes are removed and rapidly weighed on a semimicro balance (sensitivity ±0.01 mg) and then returned to the storage bottle. The weight loss is recorded. The tubes are ready for use when the rate of weight loss becomes constant (within ±2 per cent).

10. Calculations

10.1 Gaseous Sulfide

10.1.1 Determine the sample volume in liters from the gas meter or flow meter readings and time of sampling. Adjust volume to 760 mm mercury and 25°C (V_s).

10.1.2 Determine the concentration of H_2S in $\mu g/m^3$.

$$\mu g\ H_2S/m^3 = \mu g\ H_2S/V_s \times 10^{-3}$$

where:

$\mu g\ H_2S$ = micrograms hydrogen sulfide determined
10^{-3} = conversion factor, m^3/ℓ

10.2 Gaseous Sulfide from Aqueous Sulfide

10.2.1 Determine the sample volume (V) in liters from the gas meter or flow meter readings and time of sampling. Adjust volume to 760 mm mercury and 25°C (V_s), using the correction formula:

$$V_s = V \times \frac{P}{760} \times \frac{298}{(T + 273)}.$$

where:

V_s = Volume of air in liters at standard conditions
V = Volume of air sampled in liters
P = Barometric pressure in mm Hg
T = Temperature of sample air in °C

10.2.2 Using the Beers-Law Standard curve of absorbance vs. $\mu g\ S^=$ ion, determine $\mu g\ S^=$ ion in the sampling impinger corresponding to its absorbance reading at 670 nm.

10.2.3 Calculate the concentration of H_2S in the aspirated volume of air using the formula:

$$\text{ppm, } H_2S = \frac{\mu g\ S^= \times 24.45}{V_s \times MW}$$

where:

$\mu g\ S^=$ = micrograms sulfide ion (Section 10.2.2)
24.45 = molar volume of an ideal gas at 25°C and 760 mm Hg
MW = mass of sulfide ion, 32.06

11. References

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ABSTRACT

THE MEASUREMENT AND DISTRIBUTION OF GEOTHERMAL SULFUR POLLUTANTS IN THE GEYSERS AREA

L. A. Cavanagh
Stanford Research Institute, Menlo Park, California

The use of geothermal energy for the production of electricity has been viewed with increased interest as the availability of natural gas has decreased and cost of petroleum has increased. The Geysers Area is the location of ten Pacific Gas and Electric Company (PG&E) geothermal power plants producing some 502 megawatts of power. Hydrogen sulfide (H_2S) complaints frequently arise in the populated regions downwind of the area. Due to its concern that geothermal expansion would adversely affect air quality in the surrounding region, PG&E and steam suppliers have contracted with Stanford Research Institute to install and operate an air quality and meteorological monitoring network in The Geysers Area for a period of two years. The objectives of the study are to analyze H_2S distribution and the meteorological conditions that lead to episodes or intervals of numerous complaints about H_2S odors in the populated areas to the east. The network has been in operation for the first year of a two-year program analysis of meteorological conditions conducive to transport of H_2S from The Geysers Area to the populated areas to the east will be described.

ABSTRACT

FIELD DETERMINATION OF HYDROGEN SULFIDE

G. A. Frye and D. W. Wheeler
Aminoil USA, Inc., Santa Rosa, Calif.

Aminoil has been collecting and analyzing samples from geothermal wells since 1969. Due to the potential environmental impact of the hydrogen sulfide in the geothermal fluids, a continuing effort has been made to determine the sulfide concentration in the fluids. After comparing several methods for accuracy, interference of other constituents, and adaptability to field operations, Aminoil believes the silver-ion,selective electrode titration is well suited for geothermal operations.

ABSTRACT

CHEVRON PLANS FOR ON-SITE SAMPLING AND ANALYZING OF GEOTHERMAL WATERS

W. J. Subcasky
Chevron Oil Field Research Co., La Habra, California

In evaluating geothermal waters for power generation, it is important to know the composition of the fluid and how that fluid behaves when temperature and pressure are changed during processing. Chevron has designed and constructed on-site equipment to continuously sample fluid from a production stream and evaluate the fluid under various temperature and pressure conditions in either a flash mode or a binary heat-exchange mode. Some measurements to be made under various conditions are (1) composition and volume of noncondensible gases, (2) types and rates of corrosion, (3) types and rates of scale deposition on equipment surfaces, and (4) types and amounts of colloidal precipitates forming in effluents and their effect on brine reinjectivity. The presentation includes a discussion of the equipment design and preliminary plans for its use in evaluating produced geothermal water at the Heber site.

ABSTRACT

DEVELOPMENT OF A STANDARD METHODS MANUAL FOR SAMPLING AND ANALYSIS OF GEOTHERMAL FLUIDS AND GASES

E. M. Woodruff
Battelle-Northwest Laboratories, Richland, Washington

Work on the manual of standard methods began early in 1976 under ERDA-DGE sponsorship in response to needs apparent in our own programs as well as those expressed by other organizations. The scope of this program and progress to date are reported here.

The objective is to prepare a manual of recommended methods for sampling and analysis of geothermal fluids and gases which will assure accuracy, reliability and intercomparability of reported results, and to assist industry by reducing the analytic methods research required by each organization. Our approach has been to first identify properties and constituents of interest to the different aspects of geothermal energy exploration, development and utilization; then summarize available methods with comments on sample and instrument requirements and other factors which would influence selection including cost, accuracy and precision, interferences, or other limitations. This preliminary review was distributed to interested organizations in August 1976(1) for comment and additional input.

Those methods requiring verification or modification for application to geothermal brines will then be tested by a small group of participating laboratories. Finally, a manual summarizing these tests and recommendations will be published.

The preliminary review of constituents of interest and published analytic methods have been compiled in table form. During this effort, two additional data formats were developed to aid the administrator as well as the scientist in establishing geothermal

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[1] J. G. Douglas, et al., "Geothermal Water and Gas - Collected Methods for Sampling and Analysis, Comment Issue," BNWL-2094, Battelle-Northwest, Richland, Washington, August 1976.

capabilities. A graph was prepared to illustrate concentration ranges for constituents reported for geothermal brines throughout the world. Individual data points are included and although they are not completely comprehensive, the analyst can, at a glance, become familiar with expected ranges, distribution trends within ranges, and how frequently an individual constituent was included in brine analyses. To relate analytic requirements to specific objectives or tasks encountered in geothermal energy development and utilization, a matrix format has been devised. Tasks are matched versus properties and constituents with notations are incorporated to identify several analytic requirements.

This preliminary draft contains many methods and options that have not been evaluated for brine applications,however, they should serve to stimulate interaction between interested organizations and produce refinements that will result in a final working document aimed at reducing the research and decision-making burden of laboratories and industry. Two critical reviews of this work have been obtained by contract, and formulation of the analytic phase of the program is in progress.

Sampling and Characterization of Suspended Solids in Brine from Magmamax #1 Well

J. H. Hill and C. H. Otto, Jr.
University of California
Lawrence Livermore Laboratory
Livermore, California 94550

ABSTRACT

When high temperature, high salinity geothermal brines are cooled, appreciable quantities of solids precipitate. These suspended solids can cause extensive erosion and plugging in power plant components. In addition, there is considerable concern that reinjection of these solids with spent brine may plug the geologic formation adjacent to the reinjection wells. This report describes work done to sample these solids and characterize them so that processes can be devised for their removal or control.

Suspended solids produced in brine from Magmamax #1 well consist primarily of an iron-rich amorphous silica gel. A sampling apparatus to filter these solids out of high temperature, high pressure brine streams is described. Their chemical composition and physical description is discussed. Rates of production of suspended solids are given for brines flashed through nozzles and flashed in steam separators. Control of solids production by acidification to a pH <4.5 is described. At this time, control by acidification seems to offer an attractive alternative to conventional methods (filtering, settling, etc.) for removing suspended solids from spent brine prior to reinjection.

INTRODUCTION

When high salinity brine from the Salton Sea Geothermal Field (SSGF) is cooled, sparingly soluble constituents precipitate. Most of these solids remain in suspension as brine flows through energy conversion equipment. Unfortunately, process equipment handling high velocity brine and solids can be rapidly and severely damaged by erosion. Also, these solids plug valves and piping and may shorten the lifetime of reinjection wells by destroying geologic formation porosity. This report describes work done to sample these suspended solids and characterize them both physically and chemically so that problem areas can be identified and control techniques can be evaluated. This work was done with brine from Magmamax #1 well which is located in the Salton Sea Geothermal Area and operated by Magmamax Power Co. Some of the samples were taken from the San Diego Gas and Electric Co. Geothermal Loop Experimental Facility (GLEF).

Others were obtained from the Lawrence Livermore Laboratory Field Test Unit (LLLFTU).

RESULTS AND DISCUSSION

The apparatus used to collect suspended solids from high temperature, high pressure brine lines is shown in Figure 1. Originally, three sintered stainless steel filters were used in this apparatus to obtain a particle-size distribution for the solids. The pore size of the filters was 165, 65, and 10-μm. After examination of the collected solids indicated that they were composed primarily of an amorphous iron-rich silica gel, only the 10 μm filter was used. In use, the apparatus is fitted with valves and a pressure gauge so that the differential pressure across the filter can be regulated to <10 psi. Samples were taken from 10-in. brine lines by attaching this apparatus to a traversing sample probe (1). This probe is designed so that it can be inserted through a valve and traversed from one side of the pipe to the other. Thus it is possible to obtain a sample of the brine that is relatively free of solids that have collected on the wall of the pipe or around the valve. To avoid errors caused by the precipitation of solids when brine contacts the cold probe, the probe is heated by running the hot brine through a bypass before the valves on the sampler are opened.

Chemical analyses of samples of suspended solids taken from the pipeline near the reinjection well of the GLEF are shown in Table I. These results indicate that the solids are rich in Fe and Si. Minor amounts of heavy metals such as Pb and Zn are also present. X-ray diffraction analysis indicates that the iron-rich silica matrix is amorphous. Also, the heavy metals occur primarily as sulfides. These samples also contain a considerable amount of Ca and Mn which occur primarily as carbonates. Their presence is attributed to the reinjection of high pH (9 to 10) condensate into the spent brine during this period of operation.

Suspended solids taken from the brine at Magmamax #1 wellhead and from the separator on the LLLFTU were found to be almost pure PbS. Electron micrographs of these solids are shown in Figure 2. These micrographs and chemical analyses indicate that these solids are submicron sized-crystals of PbS which are cemented into larger agglomerates.

Electron micrographs of suspended solids taken from the reinjection pipeline of the GLEF are shown in Figure 3. These micrographs show the typical silica gel structure of the amorphous iron-rich silica matrix. This is the same structure previously found in silica scale deposited from geothermal brines.

The extent of solids production in the GLEF and the LLLFTU was determined by sampling suspended solids at the Magmamax #1 wellhead, the separator of the LLLFTU, the reinjection pipeline of the GLEF, and from brine which had been expanded through nozzles to atmospheric pressure in

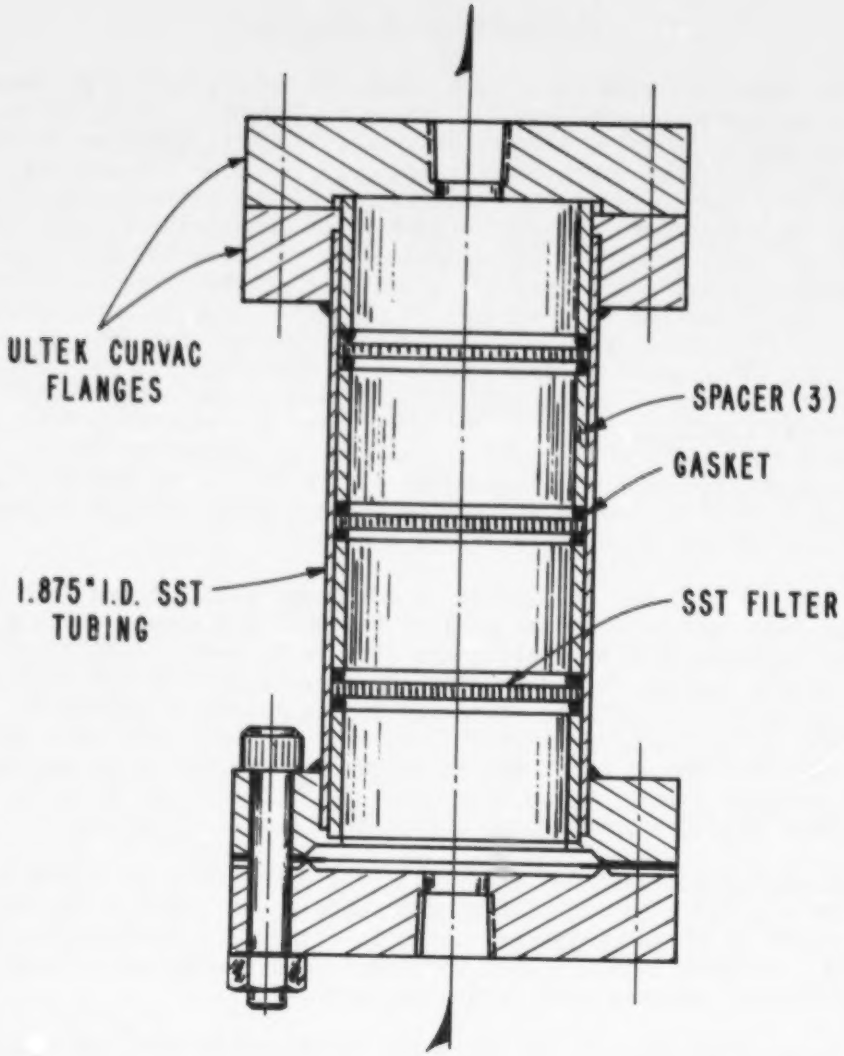
ULTEK CURVAC FLANGES
SPACER (3)
GASKET
1.875" I.D. SST TUBING
SST FILTER

Figure 1. Suspended solids sampler

90°C
150-300 psi

ELEMENT	Wt. % (normalized to 100)			
	MX-3-L12		MX-3-L14	
	FILTER SIZE		FILTER SIZE	
	65 µm	10 µm	65 µm	10 µm
Si	50	43	32	30
S	1.7	0.9	0.7	0.4
Ca	10	5.4	4.4	1.9
Mn	3.0	4.6	4.1	3.0
Fe	28	37	48	57
Cu	0.5	0.6	0.8	0.3
Zn	1.6	2.1	1.2	0.8
As	0.3	0.6	0.5	0.8
Sr	0.03	0.09	0.03	0.05
Mo	0.01	0.009	0.03	0.04
Ag	0.009	0.06	0.003	0.003
Cd	0.003	0.006	-	-
Sn	0.01	-	0.003	0.004
Sb	0.003	0.15	0.03	0.04
Ba	0.13	0.6	0.08	0.14
Pb	1.4	4.5	1.0	1.1

TABLE I. SEMI-QUANTITATIVE ANALYSIS OF SUSPENDED SOLIDS FROM THE GLEF.

Brine Sample	Concentration of Solids mg solids/kg brine	Composition of Solids
Magmamax #1 Wellhead	26	PbS
Separated Brine	20	PbS
Expanded through nozzle	475	Fe-Si matrix with minor PbS
Magmamax #3 Reinjection line from GLEF Operation	480	Fe-Si matrix with minor PbS and ZnS

For a 10-MW powerplant using 800,000 lb/hr of brine, solids production would be approximately 5 tons/day.

TABLE II. SUSPENDED SOLIDS PRODUCTION

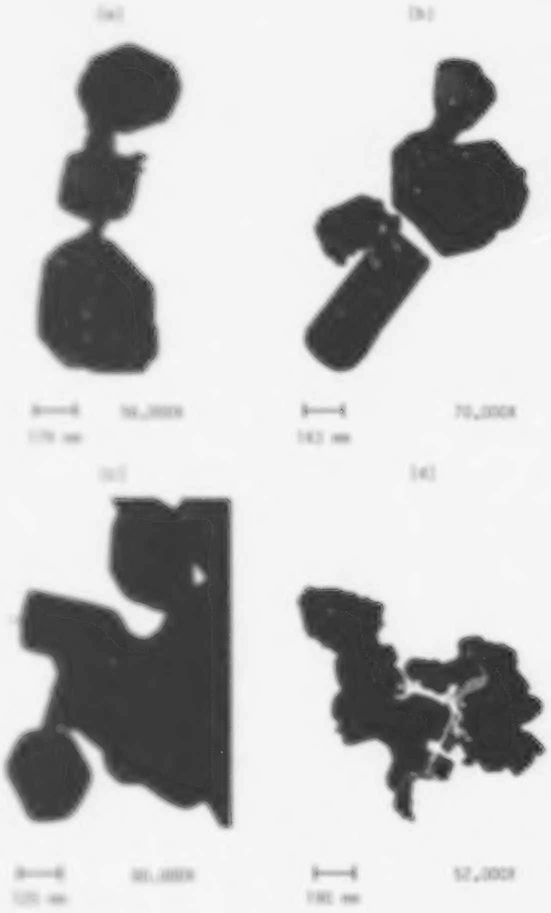
(a)
(b)
179 nm
56,000X
143 nm
70,000X
(c)
(d)
125 nm
80,000X
190 nm
52,000X

Figure 2. Electron micrographs of solids from Magmamax #1 wellhead

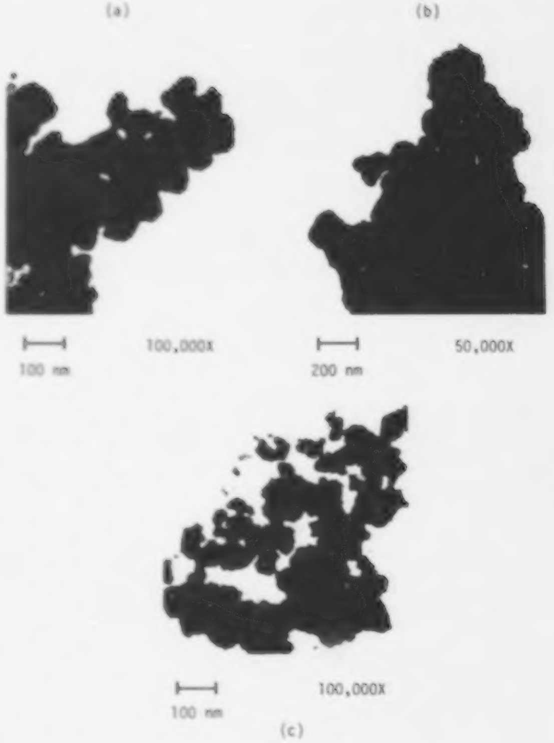
(a)
(b)
100 nm
100,000X
200 nm
50,000X
100 nm
100,000X
(c)

Figure 3. Electron micrographs of solids from GLEF reinjection line

the LLLFTU. These results are shown in Table II. These data indicate that brine from Magmamax #1 wellhead contains about 26 ppm of suspended solids. However, about 475 ppm of suspended solids are produced when brine is flashed to remove steam in the GLEF or when brine is flashed through nozzles to atmospheric pressure in the LLLFTU. For a 100-MW powerplant, 475 ppm of suspended solids corresponds to approximately 5 tons/day which would be reinjected with the spent brine.

The time elapsed before solids will plug a reinjection well depends largely on the porosity and fracturing that exists in the formation. However, there can be little doubt that plugging will eventually occur. Therefore, methods must be developed either to prevent the formation of solids in process brine or to remove solids from the spent brine. One technique that we have tried to inhibit the formation of solids is acidification.

The rate of suspended solids production in Magmamax #1 brine was determined as a function of pH during acidification experiments conducted in October and November, 1976. In these experiments, separated high temperature (220°C), high pressure (250 psi) brine was acidified and expanded through nozzles in the LLL brine modification apparatus to atmospheric pressure. Samples used to determine suspended solids production were taken from elbows in the exhaust system about 16 inches downstream from the nozzles. The temperature of the brine at the sampling point was about 95°C. All samples were transferred to a constant temperature bath at 85°C immediately after they were taken. To determine the rate of solids production, the samples were removed from the constant temperature bath at timed intervals and immediately filtered through glass frits with a nominal pore size 4 to 5.5 μm. The solids were then washed with distilled water, dried at 110°C and weighed.

Initial experiments were conducted over intervals up to 24 hrs. with samples in the pH range from 1.6 to 5.8. Results are shown in Figure 4. These data indicate that the precipitation of suspended solids from Magmamax #1 brine in this pH range is essentially complete in 4 hrs. or less. They also show that acidification of the brine to a pH <4.5 greatly inhibits the production of suspended solids. The amount of solids produced at a pH <4.5 is <1/10 the amount produced in unmodified brine (pH 5.8). These results were confirmed by additional experiments conducted over shorter time intervals.

The quantity of suspended solids produced as a function of pH in a 4-hr time interval is shown graphically in Figure 5. This figure emphasizes the decrease in solids production as the brine is acidified to a pH <4.5. It shows that over 800 ppm of solids precipitated from unmodified brine (pH ~5.8). However, acidification of the brine to a pH <4.5 reduced solids production to <30 ppm.

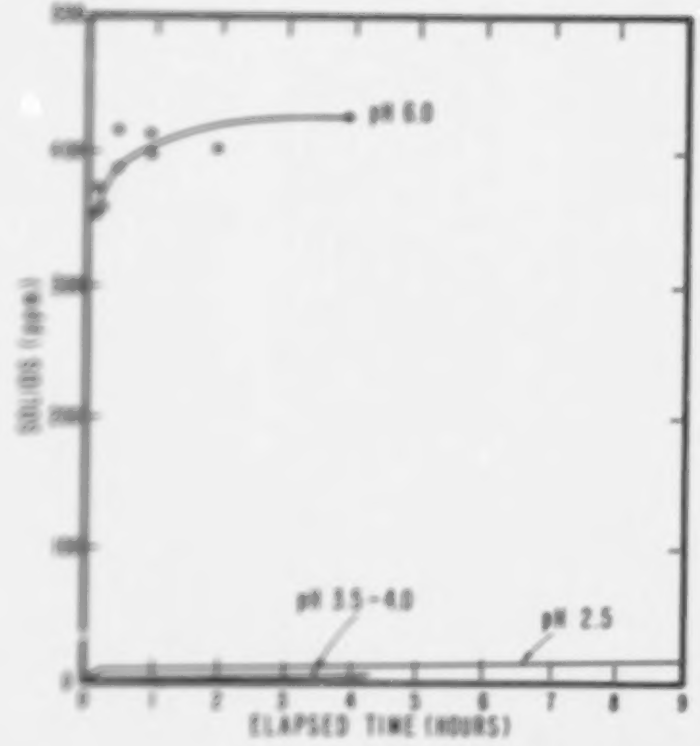

Figure 4. Rate of solids production at 85°C in separated Magmamax No. 1 brine

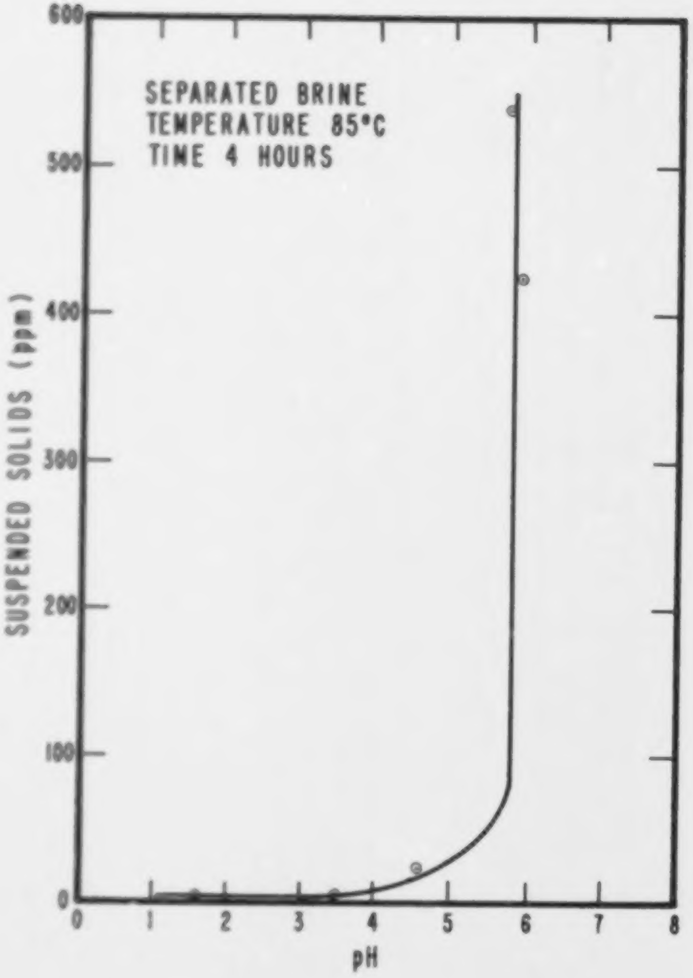

Figure 5. Suspended solids production as a function of pH

The solubility of precipitated solids in acid solutions was also investigated. In this experiment, a 5 gallon sample of brine was taken from Magmamax #1 well and allowed to cool to ambient temperature. Aliquots of the brine together with its suspended solids were then treated as shown in Table III. These data indicate that the unmodified brine contained 580 ppm of suspended solids. They also show that <1/3 of the solids redissolved when the brine was acidified to concentrations as high as 1.0 M HCl together with 0.1 M HNO_3. Therefore, it does not seem practical to remove solids from cold brine by redissolving them with acid.

Removal of suspended solids from spent brine by conventional techniques such as settling or filtration are additional alternatives. The primary disadvantage of these techniques stems from the tremendous amounts of brine that must be handled to remove relatively small amounts of solids. Also, some techniques may have adverse environmental impacts. For instance, leakage from settling ponds could destroy valuable farm land which surrounds the geothermal sites. In addition, there would be a problem associated with disposal of some solids even if most of them were processed for mineral recovery.

In conclusion, the solids produced when brine from Magmamax #1 well cools consist primarly of an amorphous iron-rich silica matrix with minor amounts of heavy metal sulfides. Acidification of Magmamax #1 brine to a pH <4.5 inhibits the formation of these suspended solids and seems to be a promising technique for the control of solids production. Because the solid-forming constituents remain dissolved in solution, they do not cause erosion and plugging of conversion equipment. Also, they can be reinjected with the spent brine. Thus, problems associated with the removal of suspended solids from spent brine and with their disposal are avoided.

ACKNOWLEDGEMENT

The authors wish to express their appreciation to the many people who contributed time and effort to this project. We wish in particular to acknowledge the work of J. P. Mahler and R. G. Grogan who designed and built the sampler, to R. Ryon who did the x-ray fluorescence analyses, to W. F. Birka who did the x-ray diffraction analyses and to L. B. Owen who furnished the electron micrographs.

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Work performed under the auspices of the U.S. Energy Research & Development Administration, contract No. W-7405-Eng-48.

Treatment	Concentration of solids after treatment[a] mg/kg brine
None	580
Acidified to pH 4.1, allowed to stand 5 hrs. at room temperature.	615
Acidified to pH 2.0, allowed to stand 5 hrs. at room temperature.	460
Acidified to pH 2.0, allowed to stand 3 hrs. at 90°C.	400
Leached 1 hr. in 1 M HCl, 0.1 M HNO_3 at 50°C.	390

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[a] All samples were filtered, washed with H_2O and dried at 110°C.

TABLE III. RESPONSE OF SUSPENDED SOLIDS TO ACID TREATMENT

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ABSTRACT

SAMPLING AND ANALYSIS OF HOT AND COLD SPRING WATERS AND ASSOCIATED ROCK AND SOIL SAMPLES FROM POTENTIAL GEOTHERMAL RESOURCES AREAS IN NORTH CENTRAL NEVADA.

H. R. Bowman, H. Wollenberg, F. Asaro and A. Hebert
Lawrence Berkeley Laboratory, Berkeley, California

The principal objective of the geochemical section of the geothermal resource assessment program at L.B.L. is to develop and evaluate new techniques and methods for sampling and analyzing materials associated with hot spring activities. The analytical methods were mainly (1) neutron-activation-analysis (NAA), (2) non-dispersive xray-fluorescence-analysis (XRF), and (3) gamma-ray-spectrometry (GRS). These methods together are capable of testing for over 50 elemental abundances in rock, soil and evaporated water samples. The methods complement one another with NAA primarily used for trace and minor elements, XRF for the more abundant elements and GRS for the radioactive elements. The rather high precisions of these methods allow considerable cross-checking of elemental abundances determined by the different methods.

The analytical results indicate that: (1) H_2S (determined by XRF) and W (determined by NAA) both correlate with down hole temperatures within a specific geothermal system; (2) the uranium daughters, determined by GRS measurements of spring waters and deposits, are most abundant in $CaCO_3$ dominated systems; (3) uranium may be concentrating at depths within hydrothermal systems.

RESULTS OF SAMPLING AND ANALYSIS OF HOT AND COLD SPRING WATERS AND ASSOCIATED ROCKS AND SOILS FROM POTENTIAL GEOTHERMAL RESOURCE AREAS IN NORTH CENTRAL NEVADA*

H. Bowman, H. Wollenberg, F. Asaro, and A. Hebert

INTRODUCTION

This work is concerned with the sampling, analytical procedures, and analytical results from a study of four hot spring areas in the Battle Mountain high heat-flow area of north-central Nevada. These areas include Kyle Hot Springs (Buena Vista Valley), Leach Hot Springs (Grass Valley), Buffalo Valley Hot Springs, and Beowawe Hot Springs (Whirlwind Valley). This effort is part of a more general study at the Lawrence Berkeley Laboratory and the University of California at Berkeley on applications of geoscience techniques to geothermal resource area assessment (Wollenberg, 1975).

We have collected and analyzed water samples from both hot and cold springs in these areas as well as rock samples from associated formations. Our sampling and analytical techniques have been described in detail earlier (Bowman, 1975, Wollenberg, 1976) and will be discussed here only briefly.

A number of water sampling methods were tried. The most reproducible results were obtained by inserting a Tygon tube down into a spring or spring orifice, drawing water up through a 0.45-micron filter and into a half-liter nalgene bottle using a hand-operated vacuum pump (Fig. 1). The half-liter water samples were evaporated in the

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*Work was performed under the auspices of the U.S. ERDA.

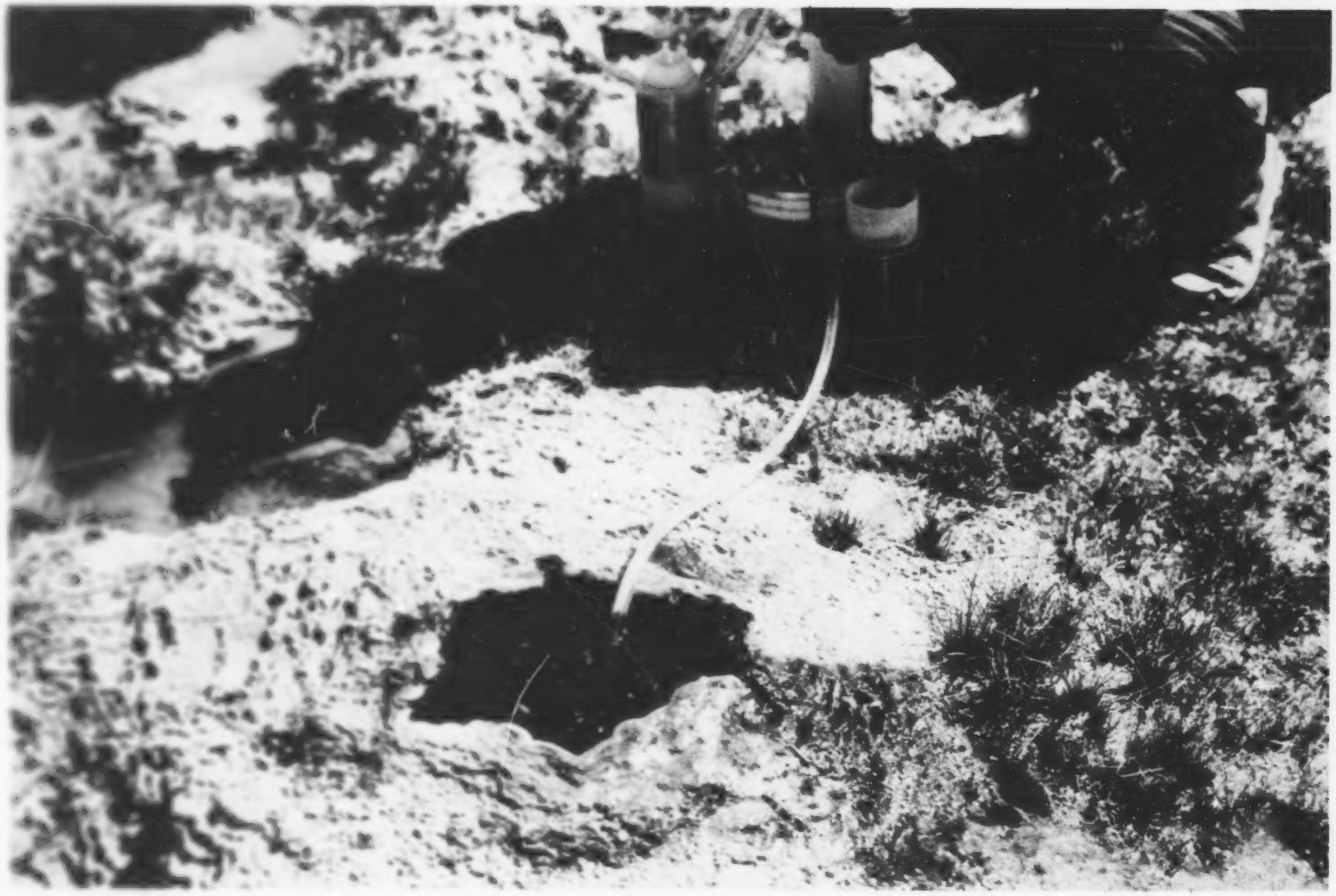

Figure 1.

laboratory (at 80°C) in the original plastic collecting bottles. These collection methods were devised to retain all solid materials, including those which would normally precipitate on cooling.

At the sites, a drop of water from each spring was evaporated onto a Lexan disk with a fixing solution. These samples were analyzed in the laboratory using soft x-ray fluorescence (XRF). A silver disk was placed in a separate sample from each spring for H_2S determination using the same XRF method (Hebert and Street, 1974).

Separate aliquots of water evaporates and crushed rocks were fused into glass disks for XRF measurements. Samples for neutron activation analysis (NAA) were prepared by mixing these materials with a cellulose binder and pressing them into small pellets (Bowman, 1973).

RESULTS

Buffalo Valley Hot Springs

Water Analysis

Four separate hot pools were sampled at Buffalo Valley Hot Springs, and the results are given in Table I. The last column in Table I gives the average abundance for the four pools along with the measured RMS (1σ) deviations. The average abundances for the elements Na, Rb, and Cs have been underlined and the (1σ) deviations are 2.2%, 3.0%, and 3.2%, respectively.

TABLE I

Buffalo Hot Springs

mg/liter

	15-6	15-1	15-4	15-5	Ave.
Temp°C	72°	72°	65°	68°	
SiO_2	75	64	81	84	76±9
Na	268	269	277	280	274±6
Cl	28	28	26	25	26.8±1.5
K	29	27	27	36	30±4
Ca	24	25	28	20	24±3
			µg/liter		
U	<.08	<.16	<.16	<.14	
Ba	160	150	140	135	146±11
W	28	30	33	24	29±4
Br	62	65	70	70	67±4
Sb	37	57	35	22	38±14
Mo	4	<1	<1	<1	
Rb	124	133	130	135	131±5
Cs	150	155	160	160	156±5
As	<10	<10	<10	25	
Fe	<100	<100	<250	<100	
Sc	<.02	<.02	<.02	<.02	
Mn	30	30	40	10	

Rock Samples

A rhyolitic ash flow unit, the Fish Creek Mountain Tuff (McKee, 1970), was sampled and the results are shown in Table II. These tuffs erupted from a center only about 10 miles south of Buffalo Valley Hot springs, in the early Miocene. Although 75 cubic miles of ash-flow material erupted, it did not spread more than about 10 miles from its source. The unit was uplifted during Basin and Range faulting and, at present, can be sampled from the bottom contact upward. The chemical compositions of the ash layers are shown in Table II with the lower ash flow sheets on the right. The errors shown in col. 1 are the 1 σ values or the precision of measurement. Accuracies can be obtained by refering to Bowman (1973).

Buffalo Valley Heat Flow Holes

Data from a heat flow hole (BV-2) cuttings, drilled just south of Bufallo Valley Hot Springs and a hole drilled about 2 miles northwest of the sprins (BV-3) are shown in Fig. 2. The SiO_2 contents for these holes are plotted as a function of hole depth. At the bottom of this figure we have plotted the temperature profile of these wells. The BV-2 data in Fig. 2 suggest that Fish Creek Mountain Tuff, or sediments from this ash, may extend down to 300 ft. at Buffalo Valley Hot Springs. The data from BV-3 indicates the presence of much more basic sediments that were derived primarily from the Tobin Range to the west.

TABLE II

Comparison of Chemical Analysis of Fish Creek Mt. Rhyolitic Tuft Sequence

	7	4	3	2	1	6A	6B	6C
SiO_2	75.08	74.00	71.23	74.70	73.74			
Al_2O_3	13.0	13.2	13.4	12.5	12.4			
Σ FeO	0.51±.01	0.28	0.87	0.64	0.65	1.34	.121	1.28
MgO	0.03	0.12	0.26	0.20	0.13			
CaO	0.80	0.57	1.86	0.47	0.47			
Na_2O	3.38±.03	4.20	4.06	4.42	2.84	2.60	2.79	2.61
K_2O	5.40	5.09	4.59	4.58	6.18	6.0	6.0	5.9
TiO_2	0.20	0.11	0.19	0.06	0.05	0.11	0.11	0.11
MnO	0.004	0.006	0.019	0.015	0.019	0.024	0.025	0.024
Total	98.40	97.53	96.48	97.54	96.50			
U	6.70±.05	11.3	13.0	16.1	23.4	20.8	22.2	21.3
Th	30.5±.2	66.8	74.5	113.5	116.3	84.2	84.7	83.3
Ta	2.01±.01	4.49	4.80	6.42	5.49	5.58	5.46	5.54
Hf	5.6±.1	10.5	10.0	10.3	9.9	10.1	9.7	10.1
La	97±1	70	59	23	27	26	29	27
Ce	180±1	137	120	50	72	66	68	67
Nd	65±2	61	60	38	51	54	66	53
Sm	9.88±.02	11.6	12.4	10.6	16.2	17.4	18.3	17.4
Eu	0.35±.02	0.18	0.29	<.01	<.01	0.09	0.06	0.05
Tb	0.84±.04	1.6	2.0	2.2	3.4	3.1	3.1	3.1
Dy	5.1±.1	9.8	12.1	13.6	21.3	21.8	22.8	21.7
Yb	2.54±.04	5.0	6.2	6.2	8.9	9.0	9.1	9.0
Lu	0.30±.02	0.68	0.76	0.80	1.12	1.08	1.17	1.12
Rb	180±4	498	495	685	884	476	481	489
Cs	4.2±.1	19	25	32	30	20	20	20
W	2.9±.3	3.3	3.5	3.8	4.3	4.6	4.4	4.2
Ba	425±20	201	330	31	105	<30	<30	<30
Sb	0.2±.1	1.0	1.7	1.6	1.7	0.85	0.75	1.06
Mo	<0.7	<.5	<.5	1.2	3.2	7.2	7.7	5.6
Sc	3.2±.1	1.8	3.7	1.7	1.0	1.9	1.4	1.8
Co	0.21±.04	0.4	1.0	0.3	0.7	0.3	0.2	0.3
Zn	56±5	100	200	140	137	130	115	80
Cr	<9	<10	<10	<10	<10	<7	<7	<7
Ni	<10	<10	<10	<10	<10	<7	<7	<7

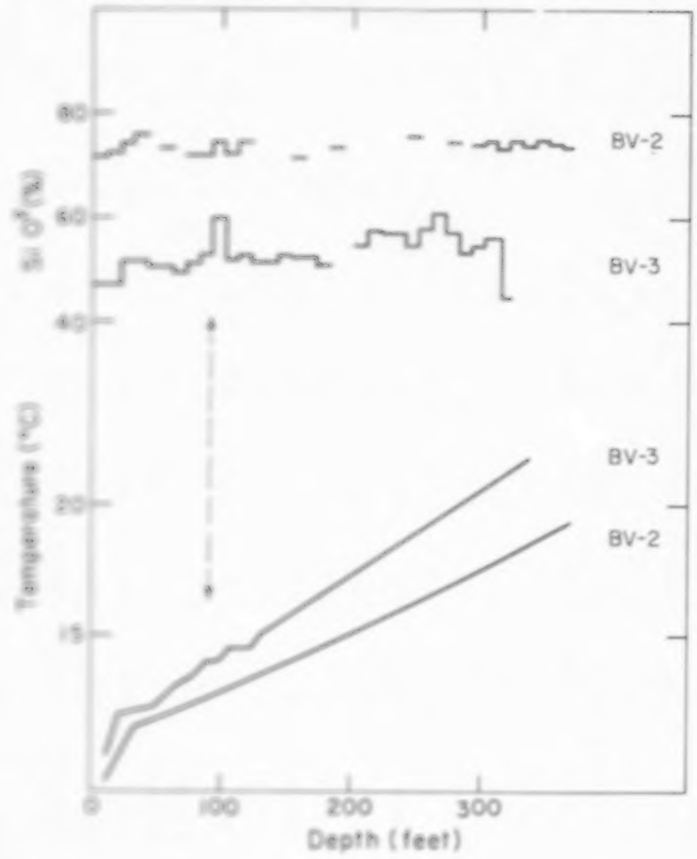

Figure 2. Buffalo Valley heat flow, holes 2 and 3

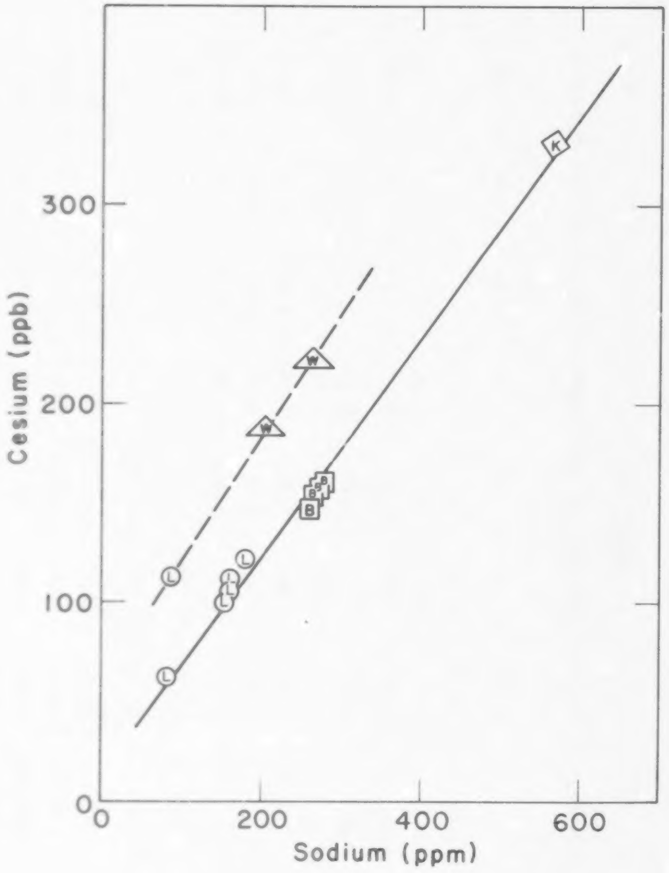

Figure 3.

The slight job in the temperature profile of BV-3 seems to be associated with the SiO_2 high of the BV-3 data above.

Grass Valley (Leach Hot Springs area)

Water Analysis

Five separate pools in the Leach Hot Springs area were sampled along with three nearby cold springs. The chemical compositions of the hot waters at Leach Hot Springs varied considerably from spring-to-spring. The cesium, rubidium and chloride content of the hot spring waters are plotted in Fig. 3 against sodium concentrations. The chloride content correlates quite well with the sodium content and a general trend can be seen in the Cs and Rb versus Na data. The spring surface temperatures are inversely related to the Na and Cl contents of these waters.

DISCUSSION

The overall cesium and sodium data for all hot springs are plotted in Fig. 4. The Buffalo data (B) seems to line up with the Kyle data (K) and most of the Leach data (L). The maverick pool at Leach seems to be off this line as are the two data points from Beowawe (W).

The data from Buffalo Valley seems to follow this general trend and although the variations are small they may be real. The significance of these correlations is not understood at present and is being studied.

The overall tungsten data is shown in Fig. 5. The tungsten abundances in hot and cold spring waters are plotted on the vertical

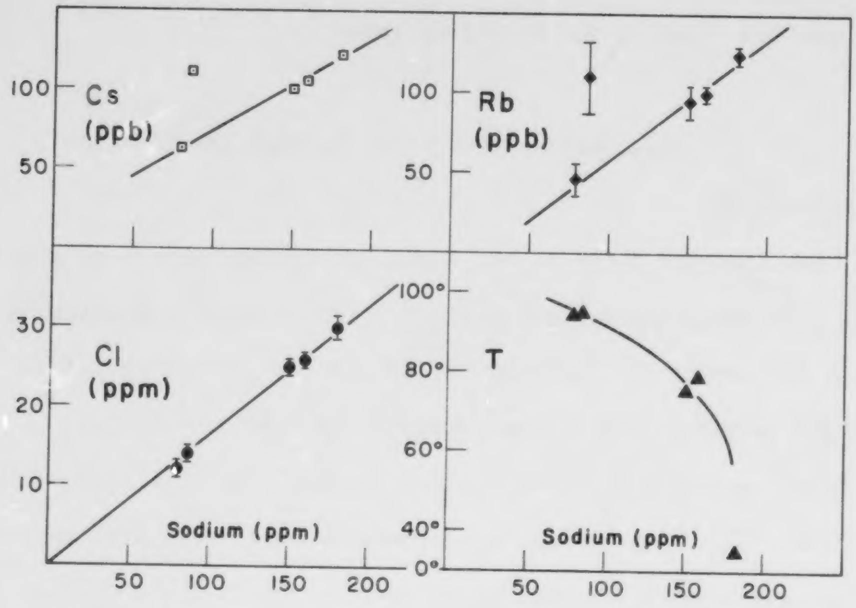

Figure 4. Leach Hot Springs.

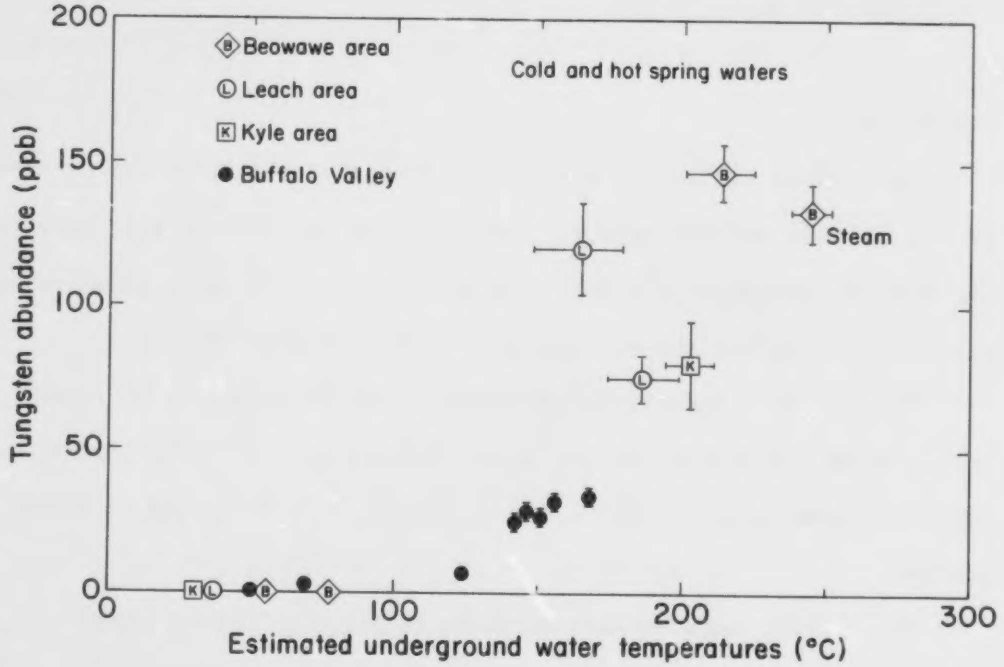

Figure 5. Cold and hot spring waters.

scale and calculated aquifer temperatures are shown along the horizontal axis. Not much is known about the tungsten rock-water interactions, but these data suggest that tungsten prefers the liquid phase at elevated temperatures.

The H_2S dissolved in these waters was tested by placing a silver disk into bottles of spring water and then testing for sulfur later by using XRF. The dissolved H_2S seems to vary with the calculated aquifer temperature (Fig. 6) suggesting that it may be a useful chemical geothermometer.

The uranium concentrations measured in both hot and cold springs for this region are shown in Fig. 7. The hot spring areas are labeled at the top of the figure. The bars labeled C are cold springs, and those labeled H are hot springs. The higher uranium concentrations are associated with the cold springs and not the hot. If we assume that the cold ground waters in these areas are feeding the hot spring aquifers at depth, then we must conclude from these results that the uranium is accumulating at depths. The radon contents of the hot water at Kyle and Buffalo Valley Hot Springs (Wollenberg, 1974) seem to reinforce these conclusions. Data such as these can be used to make estimates on the amount of uranium that might have accumulated at depths as well as the ages of the hot spring areas.

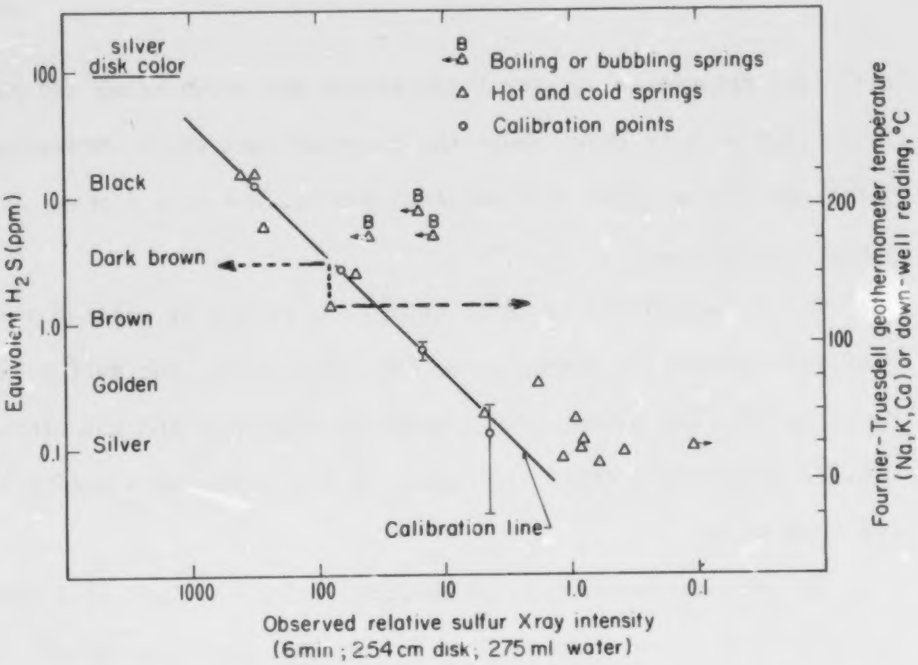
silver
disk color
B
Boiling or bubbling springs
Hot and cold springs
Calibration points
100
10
1.0
0.1
Black
Dark brown
Brown
Golden
Silver
Equivalent H2S (ppm)
B
B
B
Calibration line
200
100
0
Fournier-Truesdell geothermometer temperature
(Na, K, Ca) or down-well reading, °C
1000
100
10
1.0
0.1
Observed relative sulfur Xray intensity
(6 min ; 2.54 cm disk; 275 ml water)

Figure 6.

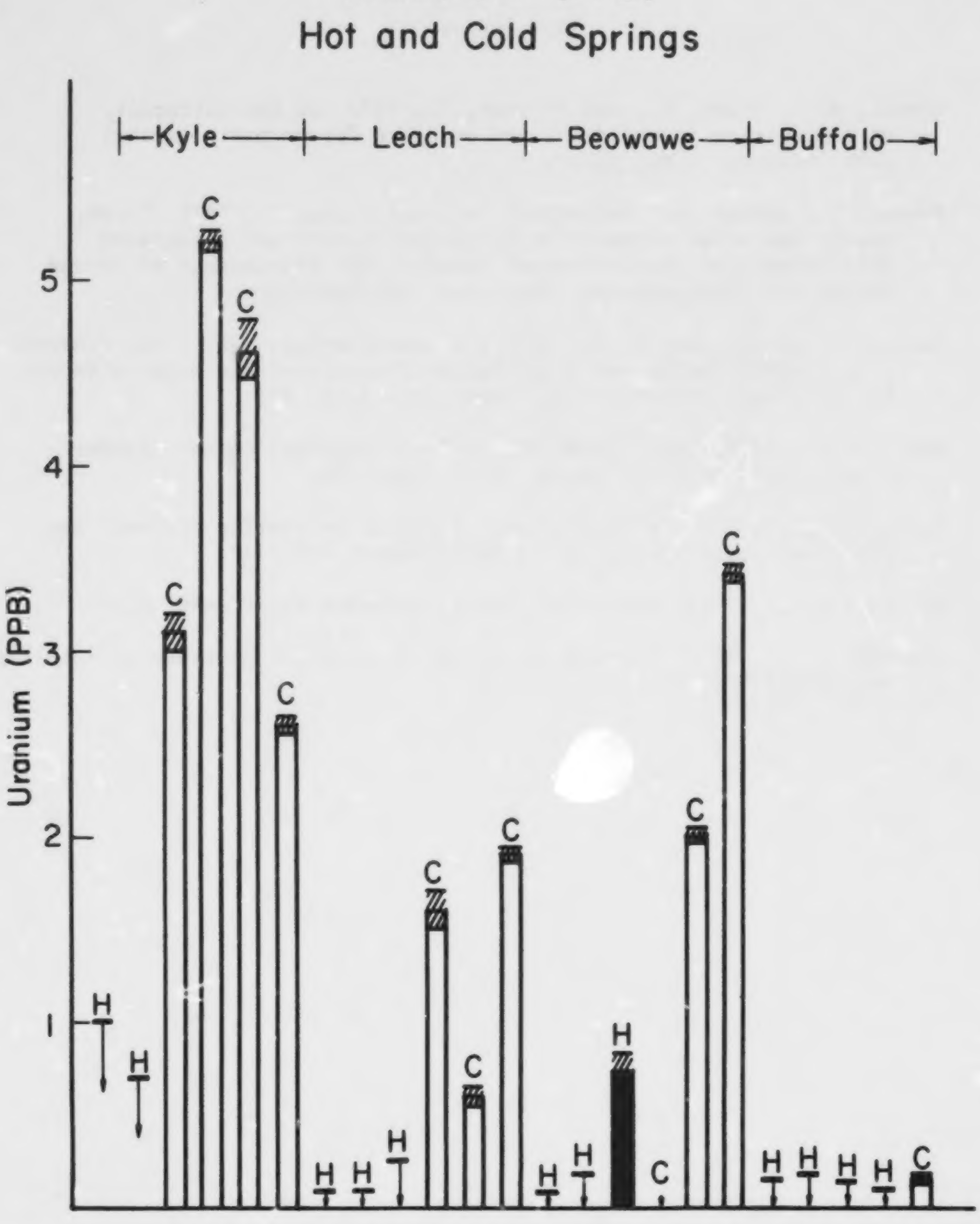
URANIUM (PPB)
Hot and Cold Springs
Kyle
Leach
Beowawe
Buffalo
Uranium (PPB)
1
2
3
4
5
H
C

Figure 7.

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ABSTRACT

METHODOLOGY FOR SAMPLING AND ANALYSIS OF HIGH PRESSURE STEAM LINES

W. Hamersma
Systems Group of TRW Inc., Redondo Beach, California

This paper is based on work at TRW which developed methodology for sampling and analysis of energy and synthetic fuel plants for an environmental assessment.

An experimental approach and plan will be presented adapted from existing technology for the sampling and analysis of high pressure steam lines. The sampling apparatus will allow for the collection of fluids and non-condensable gases at atmospheric temperature. An analysis scheme for these fluids and gases will be briefly described.

The sampling portion of this plan will be adpted from Chapter V of "IERL Procedures Manual: Level 1 Environmental Assessment".

ABSTRACT

HOW CAN STANDARD METHODS FOR SAMPLING AND ANALYSIS SUPPORT THE MOTIVES BEHIND THE REGULATIONS?

D. E. Michels
EG&G Idaho, Inc., Idaho Falls, Idaho

The basic concern about geothermal effluents lies in their potential detriment to the biological community. Thus, we need good regulations for real protection. Of course, regulations about the effluents would be foolish if they turned out to be irrelevant to ecological health. Unfortunately, basing measures of regulatory conformance on real biological effects risks demonstrating facts too late.

Environmental sampling can give earlier warnings about ecological harm, but relies on abstract models. On one hand these models relate environmental contaminations to biological effects. On the other hand they require special concepts of sampling and data interpretation to yield data usable for the models of bio-effects. Basing regulations on these models, sampling concepts, and interpretational methods leads to a judgemental jungle about whether factors are over- or under-emphasized. This in turn can lead to acrimonious debate over whether regulations about environmental contaminations are either relevant or actually being met.

The least ambiguous place to measure effluents is at the source and there is some practicality in enforcing regulations on such measures. However, it may be an indefinite path from an effluent to a biologic effect. Thus, effluent regulations are at a great risk of being inappropriate.

Effluent sampling, environmental monitoring, and bio-effect measures have distinct methods of collecting data and interpreting it. Partly, these result from the different aspects of the media, but also because the motives for taking samples are different. Parallel with these different motives, value judgements about merit differ among workers. These differences can lead to conflict about whether a (proposed) regulation is appropriate.

How might regulations be developed so as to be judged fair and relevant to all three points of view? Could one point of view be accepted as philosophically superior? Could standard methods of sampling and analysis be chosen with respect to how the data will be interpreted?

HOW CAN STANDARD METHODS FOR SAMPLING AND ANALYSIS SUPPORT THE MOTIVES BEHIND THE REGULATIONS?

Donald E. Michels
Idaho National Engineering Laboratory

INTRODUCTION:

Three kinds of questions relate to standard methods for sampling geothermal fluids:

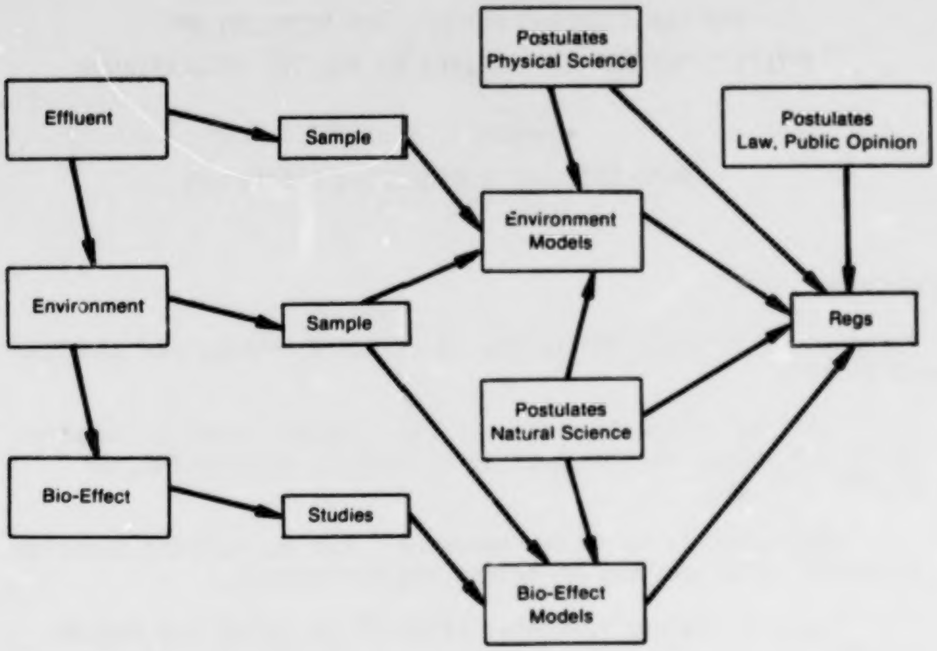
> "What is it like?" (posed in the academic sense of inquiry about the phenomena irrespective of social, engineering, or health effects),
>
> "What will it do to the hardware?" (an engineering question concerned with features of design and economics),
>
> "What is the environmental effect?" (a social and health issue).

The requirements and techniques are different for each evaluation and, to a possibly serious degree, workers asking one of the questions above may not fully hear the other questions or their answers.

The drive to establish regulations and the need to support enforcement with standard methods concern the last item. Curiously, only a few of the methods presented at this meeting so far apply to measuring environmental effects. Environmental measures deserve more attention, not only because of health and environmental issues, but also because such monitoring will be a significant overhead cost item on operational systems, irrespective of how well the installations may be accepted by the public. It is important that both the regulations and the sampling/analysis (R&S/A) be biologically astute. The intent of this presentation is to show the kinds of information needed. Additional work will be required to identify specific R&S/A that are both effective and low-cost.

INPUTS:

The construction of regulations requires input of several kinds, as diagrammed in Figure 1. We perceive effluent materials getting into the environment to an extent that the amounts picked up by biota might have detrimental effects. Thus, our ultimate concern is biological. The environmental concentrations, tissue concentrations, and bio-effects are indirectly connected to effluent regulations. Data obtained from studies


Postulates
Physical Science
Effluent
Sample
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Law, Public Opinion
Environment
Models
Environment
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Regs
Postulates
Natural Science
Bio-Effect
Studies
Bio-Effect
Models

Figure 1. Flow sheet for regulations

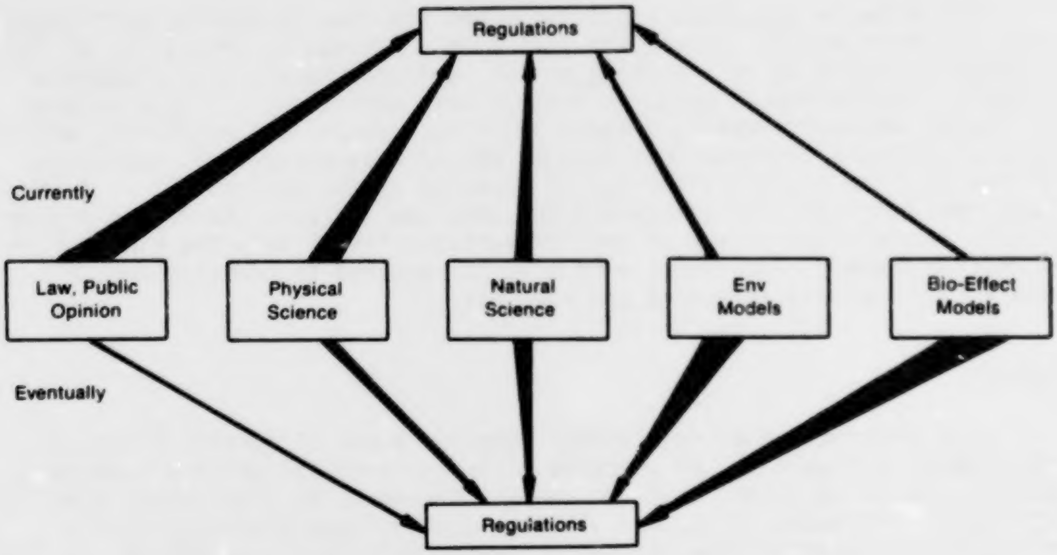
Regulations
Currently
Law, Public
Opinion
Physical
Science
Natural
Science
Env
Models
Bio-Effect
Models
Eventually
Regulations

Figure 2. Inputs to regulations

of the effluent, environment, and bio-effects need to be incorporated into models. Those models, combined with informed judgement (postulates), might yield regulations that are fair and effective because of being biologically astute -- if the several inputs are well-balanced.

Figure 2 shows two ways in which the inputs to regulations might be balanced; the widths of the several arrows indicate the relative weighting. The upper part shows my current perception of how the inputs have been apportioned; the lower part is my suggestion for how they should be. I won't insist that the widths of all the arrows are exactly right, but there are three points worth making in this regard: 1) we do not now have an optimum apportionment, 2) an optimum apportionment would still be diagrammed by arrows of unequal width, and 3) the optimum input would emphasize models of environment and bio-effect.

These models deserve to be elaborated so as to show the kinds of thought processes used to deal with the transfer of toxins between environmental compartments, since some of those compartments are accessible for monitoring.

ENVIRONMENTAL PATHWAYS

Effluents eventually get into man and other species through a sometimes intricate sequence of transfers that have come to be called environmental pathways. Figure 3 shows a diagram of such a network[1]. Each box in the diagram represents an environmental compartment, each arrow a transfer between compartments. Such a diagram can be quantified by sampling which leads to estimates of effluent (concentrations, amounts, etc.) in the separate compartments and possibly the rates of transfer. Some compartments are less difficult to sample than others so that an S/A program might focus on them. Unfortunately, the easier sampling tends to be toward the left side of the diagram while the items of interest, man and what he ingests, are toward the right side.

It is sometimes a long environmental path from effluents to man so that sampling effluents risks obtaining data that are ambiguous. The precision gained in sampling the upstream compartments can be dissipated by uncertainties in the transfer coefficients between the downstream compartments leading to man. The tradeoffs regarding which compartments to sample require careful weighting when setting up regulations intended to protect the biota, and man in particular.

Our attention to effluents and environmental compartments provides only a means to an end. Figure 4 shows that the effluent materials may get involved as nutrients, poisons, carcinogens, and mutagens. More specifically, the effects may be identified with primary biologic functions, cell development, or the nervous system. These latter aspects comprise our real concern. The upstream compartments and transfers are,

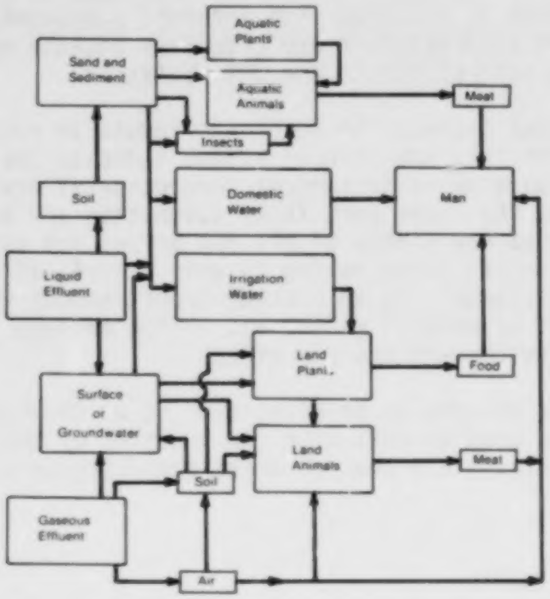
Aquatic Plants
Sand and Sediment
Aquatic Animals
Meat
Insects
Soil
Domestic Water
Man
Liquid Effluent
Irrigation Water
Land Plant
Food
Surface or Groundwater
Land Animals
Meat
Soil
Gaseous Effluent
Air

Figure 3. Pathways to man.

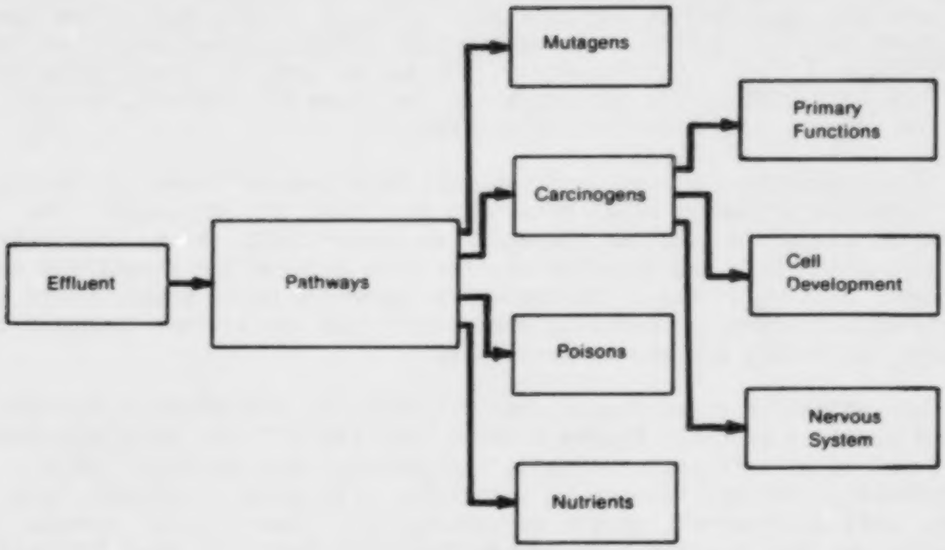
Mutagens
Primary Functions
Carcinogens
Effluent
Pathways
Cell Development
Poisons
Nervous System
Nutrients

Figure 4. Bio-effect models

in this sense, incidental to these bio-effects. We study the upstream factors to learn which pathways are amenable to control efforts that might be effective in short-circuiting or avoiding dangerous materials. We should be careful not to lose sight of this aspect of our studies. Even though effluent measurement risks being irrelevant or excessively remote from bio-effects, a thorough study of the bio-effects in real time risks learning too late what we need to know. These are the most compelling reasons to follow effluent sampling with pathway analysis.

TRANSFER COEFFICIENTS

An important concept for transfers through the environmental pathways is the discrimination factor (F)[2]. Ideally, it is defined as the ratio of concentrations (C_u, C_d) in compartments that are adjacent in the upstream-downstream sense.

$$F = \frac{C_d}{C_u} \qquad \text{eq. 1}$$

This equation has an appealing simplicity for it appears that the factor F might be measured in one place and then applied elsewhere. In the new place, the concentration in one compartment might be estimated by measuring the concentration in an adjacent compartment and multiplying by the imported discrimination factor (or its reciprocal). Unfortunately, this approach, which is useful in liquid-liquid chemical systems, for example, does not work well in the environmental context. There are at least three reasons: 1) There is no micro-reversibility in the environmental systems. For example, a cow eats grass and the gut exchanges nutrients and other chemicals, but the exchange is only one way -- none gets directly back to the living grass; 2) The feedback which does occur is cyclical, not back and forth -- the cow's feces enter the soil compartment and its decomposing organisms before part returns to the grass which is then eaten in a subsequent cycle; 3) Within any one compartment the input-output involves more than one neighboring compartment, in contradiction to the form of equation 1.

QUANTITATIVE FEATURES

Still, we need to know the buildup of toxic materials in downstream compartments and this involves some kind of data reduction. The buildup would be well described by quantifying a selected small number of features. 1) a central value for concentration, roughly or perhaps exactly an average value, 2) a measure for the range of concentrations as they occur throughout the small parts of the compartment irrespective of dispersion patterns, 3) the full inventory of effluent material that resides in a compartment, 4) estimates of precision vs. accuracy and 5) changes in the above related to dynamics of the situation and passage of time. Elaboration of the above concepts would require much more space than is available here, so I will deal with some of the important subtle factors.

AVERAGE CONCENTRATION

The abstract concept of average concentration applied to an environmental compartment usually is difficult to match with reality and adapt to the physical problems of obtaining representative samples, as the following discussion will show. Definition of average concentration (C_{avg}) relates to both the full inventory (I) of the component and the entire volume (V) of the compartment.

$$C_{avg} = \frac{I}{V} \qquad \text{eq. 2}$$

The sampling problem arises because of real variations in concentration that occur throughout the compartment. A single sample, however well-analyzed, gives no clue in itself about how well its concentration matches the average for the whole compartment. Several samples can show a pattern of concentrations, and features of the pattern may be compelling for decisions about how C_{avg} is to be derived from the several data.

The simplest approach is simply to average the analytical concentrations and propose that it equals C_{avg} as in eq. 3.

$$C_{avg} = \frac{1}{n} \Sigma C_i \qquad \text{eq. 3}$$

This method is commonly used and commonly is not valid. Most significantly, it presumes that each C_i represents a uniform fraction of the environmental compartment and that all fractions are represented fairly at the time of sampling. Such a situation can be set up in sampling a water discharge where a device extracts a pre-selected small volume of water at intervals corresponding to the passage of a much larger increment of flow. This kind of proportional sampling is more difficult in natural systems. Air sampling, for example, appears to be proportional, but seldom is. Even at a constant volume rate of filtering air the wind vectors around the sampler vary with time so that faster moving air masses are undersampled compared to their slower moving counterparts. This kind of problem might be accommodated mathematically by weighting factors (W_i). These represent fractions of the compartment which are represented by a C_i as in equation 4.

$$C_{avg} = \frac{1}{\Sigma W_i} \quad \frac{1}{n} \Sigma W_i C_i \qquad \text{eq. 4}$$

This kind of weighting may be fair, but it does imply that one must acquire some number to represent the volume (or mass) of the compartment. That number would correspond to V in eq. 2.

BACKGROUND

The notion of sampling contaminated compartments implies getting two kinds of samples -- those dosed only with a pre-existing (background) amount of the material of interest and those which are dosed with both background and the effluent. The higher analytical values might be easily recognized as contaminations, but there may be substantial trouble in making a convincing identification of low-level contamination in the face of a variable background. Points at issue may involve either or both the dimensions of the infected area and the concentration level which best divides the contaminated group from the uncontaminated. The statistics of mixed distributions apply here. The increment of contaminant inventory that hangs in the balance during disputes over the true value of background can be large since the volumes of involved soil, air, or water are often huge.

STATISTICAL APPROACHES

Some statistical methods are useful in sorting heterogeneous distributions into their homogeneous components[3]. The latter are characterized by specific central values* and measures of dispersion (standard deviations). In applying these methods to environmental cases the standard deviation should not be identified as an error term, although of course it does contain the errors. More importantly, it gives a measure of real variations in the environmental concentration from place to place. These natural variations tend to be very large in relation to the average concentration, particularly for those materials which are especially scarce. They often are large compared to analytical errors; hence the justification for ignoring error at this stage of the interpretation.

For most trace materials, Gaussian statistics (the normal distribution) are a poor model[4]. Often, better results are obtained if the data are transformed mathematically before matching to the Gaussian distribution. Among the several possible transforms the logarithmic has advantages of being both simple and broadly useful. That is, the logarithms of many data sets are distributed in (or near) a Gaussian way even though the untransformed data are not. Many standard statistical treatments can be applied to the transformed data with no further concern for validity. After the statistical treatments, the original units of the data can be restored to the calculated measures by taking inverse logarithms.

Graphical procedures are simple to use in identifying distribution mode[5] and for deciding how to unmix distributions[3]. These work well for small sets of data (12 to 200 points), but become increasingly tedious for larger sets. Computer programs which perform a digital version of the graphical procedures can be prepared[6].

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* median, mode, arithmetic average, geometric average, and others are all useful measures of central value, but statistical treatments and extensions to inventory, flux, etc., demand a proper selection of central value to yield valid results.

CONTAMINANT FLUX

Assessment of inventories may be approached through fluxes by equating inventory (I) to the algebraic sum of inputs (Q_I) and outputs (Q_O). The inputs and outputs can be incremented as in equation 5.

$$Q_I = E \Sigma C_i M_i \qquad \text{eq. 5}$$

There, M_i represents the mass of the i^{th} increment of input. The factor E represents an inefficiency for a transfer, i.e., its value is less than unity. An example involving E is given by the feed eaten by a cow. Although the entire feed mass is at some time contained within the cow, only a portion becomes part of the cow's tissues. This kind of partitioning applies also to the trace materials which are incorporated in feed as effluent contamination. Thus, the input-output approach requires a background of special studies that give estimates for E-values. E-values are less straightforward to measure than first appearances might suggest. Besides the mechanical and analytical problems in setting up a balance sheet and collecting data about feed-in and feed-out, one has to deal with interactions. That is, a value of E for a particular effluent material involves more subtle factors than chemical composition of the effluent and biologic species. General dietary balance is known to affect uptake of trace elements which are imperfectly similar to essential elements[7].

Relating effluents to feed inputs of foraging animals involves still another wrinkle. They are selective feeders -- when they can be selective. Figure 5 shows the distribution of botanic families obtained from systematic sampling of the rumen contents of steers grazing freely in a botanically limited area[8]. Contaminants are dosed differently on the several species involved, with the result that the ingestion rate for a contaminant varies seasonally. Note in Figure 5 that the seasonal variation is imperfectly aligned with the calendar. Estimating inputs to foragers by sampling feedstock species implies that the human samplers discriminate in much the same way as do the foragers. This is to say that, since foragers, like cattle, are non-random samplers, their human counterparts should be non-random also. Mimicking the selectivity exercised by foragers requires a great deal of observation. It is important to do because in some cases, the bulk of an annual dose to an animal comes in just a few months from one or two species of feed[9]. This kind of complication, once understood, and quantified, might be used to streamline effluent impact monitoring. Time and money spent sampling plant species, etc., could be apportioned according to relevance for inputs rather than according to physical prominence.

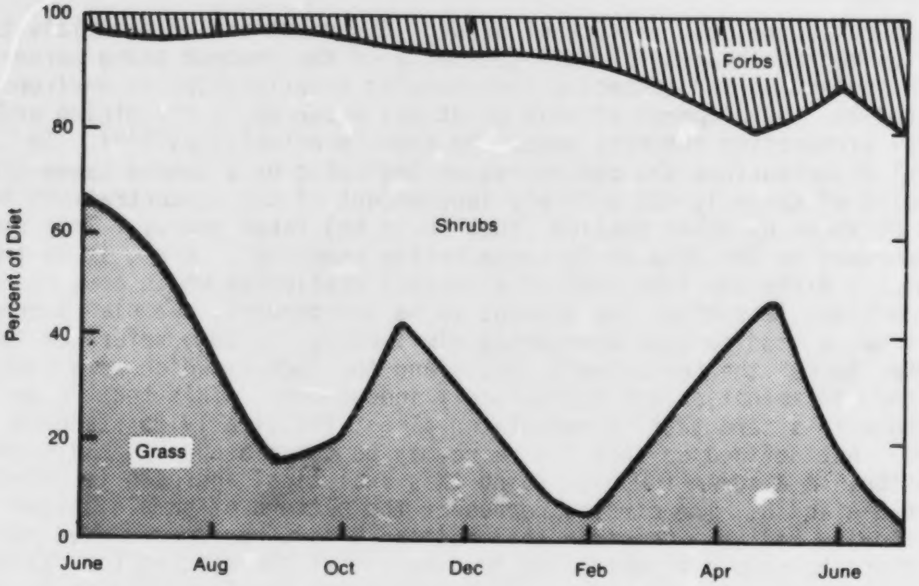

Figure 5. Botanical composition of rumen content from fistulated steers grazing on area 13, Nevada Test Site (from Ref 9 by permission)

GEOSTATISTICS

There is one more feature of natural distributions of materials that deserves mention because of both obscurity of the concept among workers and the potential for enhancing cost-benefit relationships in environmental studies. Development of this point has occurred in the mining and mineral prospecting industry under the name "geostatistics"[10]. In natural distributions the concentration indicated by a sample taken from one point of space is not entirely independent of the concentrations that might be shown by other samples (that could be) taken nearby. This notion is important to the idea of "representative sampling". Also, it is fundamentally different from most of classical statistics which have resulted from defining (assuming) the samples to be independent. Samples taken across space tend to show decreasing similarities to some reference sample. In other terms, the contaminant levels and the factors which were involved with the contamination are increasingly independent. This feature can be handled with a term that is calculated almost identically to standard deviation, but defined so that its value may be correlated with a distance dimension. A diagram for describing this analytical approach is shown in Figure 6 A and B. The circles represent the pattern of sample points in a stationary medium. Consider that pattern B is superimposed over pattern A so that the sample points coincide except that the spacing for pattern A is twice as great. Each interior sample point has four nearest neighbors. These can be compared to the central point by their difference in concentration. There is a characteristic difference which would be calculated in a statistical style by squaring the individual differences, summing, and averaging as in equation 6.

$$\sigma^2 = \frac{1}{n} \Sigma (X_c - X_i)^2 \qquad \text{eq. 6}$$

In this application X_c is successively each interior point so that the entire summation involves about 4n terms in $(X_c - X_i)$. Thus, equation 6 could be represented alternatively as in equation 7.

$$\sigma^2 = \frac{1}{4n} \sum_{c=1}^{n} \sum_{i=1}^{4} (X_c - X_i) \qquad \text{eq. 7}$$

The same calculational procedure could be applied separately to pattern A and B but the outcomes, σ-values, will be systematically different. One expects $\sigma_A > \sigma_B$ and the difference is related more to the systematically closer spacing of sample points than to the edge difference of the patterns plus random errors. The difference $\sigma_A - \sigma_B$ and the different spacings are potent descriptors of the dispersion and are called variograms. There are several classes of variograms and some are represented in Figure 7; the contexts are described elsewhere[10,11].

The implications for economic sampling shall be described with the proviso that sampling with separation in time for a flowing mass (like a river or free air) can yield a variogram as does sampling across space for stationary media. Economy is favored by longer separations between

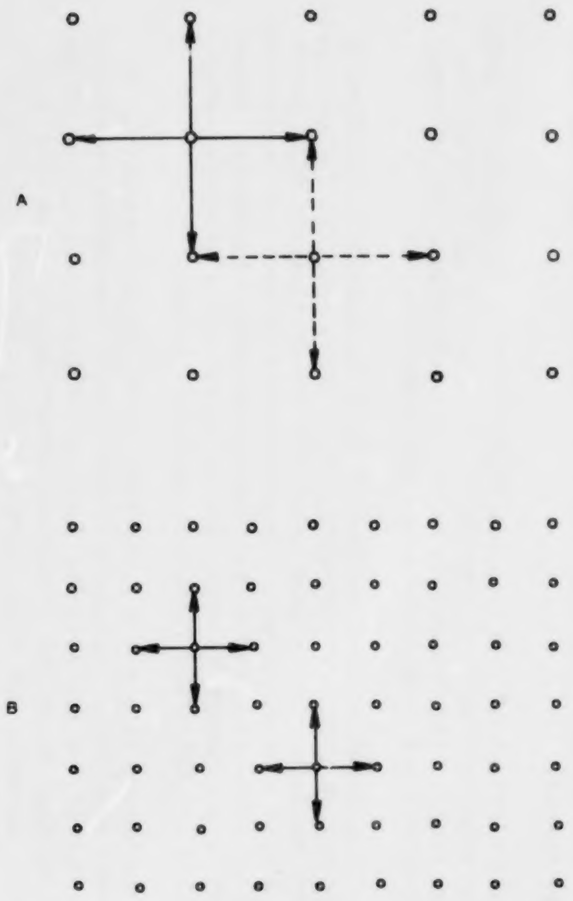

Figure 6. Geostatistics

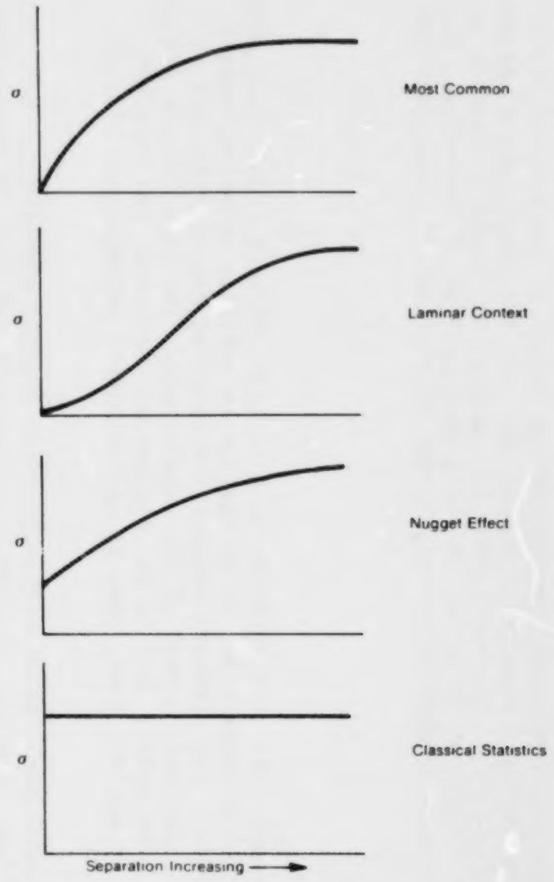

Figure 7. Classes of variograms

samples; however, one makes the separations larger at the risk of having poor representivity for material identified with the middle spaces between samples. In terms of the variogram, the separation should correspond to an interval taken rather far up on the sloped portion of the curve. Smaller separations are somewhat redundant, larger separations are less representative.

SUMMARY

In summary, the driving force to establish effluent regulations comes from both public concern and an obligation to minimize undesired environmental effects. The standard methods for sampling and analysis are required for legal enforcement of the regulations. The sampling and analysis of concern here relate less to the geothermal phenomena, and hardware engineered to exploit them, than to environmental pathways and biologic effects.

The direct sampling of effluents could greatly simplify the enforcement objective. However, it seems reasonable to ask that the regulations be astute in the biologic sense, since such is the focus of concern. Between effluent and biologic effect lie environmental pathways through which the contaminants move. The astuteness of regulations can be judged by how well knowledge about pathways is both integrated into regulations and adapted to the environmental sampling -- while avoiding problems with interpretational models.

The descriptions of pathways and their relative importance in terms of effluent materials getting into the biota require quite extensive specialized study. There seems to be no easy substitute; astute regulations require input from pathway and bio-effect studies.

Dispersion patterns presumably will be investigated by sampling at selected points in time and geography. Regulatory sampling for effluents implies that methods will be used which sharply distinguish background from only slight contaminations. Interpretation of the data in this regard requires somewhat uncommon statistical methods. Additional interpretive models are needed to track the effluents since processes which disperse them are not truly random or uniformly potent.

Representivity is a troublesome feature to demonstrate easily in environmental sampling. One approach that can be convincing involves identification of, in the distributions, of patterns that can be related to mechanisms that drive the dispersion of effluents. Such models of environmental dynamics and their counterparts in bio-effects deserve to become the dominant technical input for the regulation of effluents.

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A REVIEW OF THE CHEMICAL COMPOSITION OF GEOTHERMAL EFFLUENTS

F. Tsai, S. Juprasert and S. K. Sanyal
Geonomics, Inc., Berkeley, California

INTRODUCTION

This report presents a literature survey on the chemical composition of geothermal effluents. We have tried to cover as wide a geographical area as possible in the hope of getting a general idea of the concentration ranges of various constituents. The geothermal areas considered in this report are from New Zealand, Japan, Italy, Iceland, USSR, Central America, Mexico and the United States. The data were obtained mainly from published sources. We realize that it is difficult to make a meaningful comparison of the chemistry of the geothermal effluents from various parts of the world, because on one hand the surface and subsurface environments may vary drastically from place to place, and on the other hand the techniques of sampling and analysis of effluents may be different in different reported cases. It is conceivable that some of the data reported in the literature are in error.

REVIEW

Tables 1 and 2 show all the chemical constituents reported to have been found in geothermal effluents with their minimum and maximum concentrations and some of their significant environmental impacts. It can be seen that, in general, the chemical composition of geothermal effluents covers a very wide range, in terms of both the number of chemical elements or groups present and their concentrations. For example, the total dissolved solids (TDS) range from 50 to 400,000 ppm and pH from 1 to 10 units. From the environmental impact point of view the geothermal waters can vary in character from entirely benign and potable to highly corrosive and saline.

The constituents can be divided into 4 groups according to their relative abundance (see Table 3). The "major constituents" are the most concentrated and commonly found in geothermal systems and play the most important role in chemical reactions occurring in the system. The "secondary" and "minor" species also participate in the chemical reactions but with smaller roles. Trace elements contribute very little to the chemical reactions in the system but may have considerable implication in environmental impact. For example, trace elements such as Ni, Zn, As, Rb, Sr, Ba may be harmful to plant and animal life; most of the heavy metals are involved in formation of scales in pipes.

TABLE 1

CHEMICAL COMPOSITION OF GEOTHERMAL WATERS

Constituent	Concentration in ppm	Comments
Aluminum (Al)	0 - 7,140	
Ammonium (NH_4)	0 - 1,400	
Arsenic (As)	0 - 12	Health hazard
Barium (Ba)	0 - 250	Human death if >550mg dosage
Boron (B)	0 - 1,200	Detelerious to plants
(HBO_2)	13.6 - 4,800	
Bromide (Br)	0.1 - 3,080	
Cadmium (Cd)	0 - 1	Toxic to fish if >0.2ppm
Calcium (Ca)	0 - 62,900	Clogging scale
Carbon Dioxide (CO_2)	0 - 490	Clogging scale
(HCO_3)	0 - 10,150	pH control
(CO_3)	0 - 1,653	
($HCO_3 + CO_3$)	20 - 1,000	
($CO_2 + HCO_3 + CO_3$)	15 - 7,100	
Cesium (Cs)	0.002 - 22	
Chloride (Cl)	0 - 241,000	Major corrosion constituent
Cobalt (Co)	0.014 - 0.018	Toxic to life if large amount
Copper (Cu)	0 - 10	Health hazard if >1ppm
Fluoride (F)	0 - 35	Healthy if <1.5ppm
Germanium (Ge)	0.037 - 0.068	pH control, corrosion-scale agent
Hydrogen Sulfide (H_2S, total)	0.2 - 74	

Chemical Composition of Geothermal Waters, cont'd.

Constituent	Concentration in ppm	Comments
Iodide (I)	0 - 105	
Iron (Fe)	0 - 4,200	May precipitate on oxidation
Lanthanum (La)	20	
Lead (Pb)	0 - 200	Cumulative poison
Lithium (Li)	0 - 300	
Magnesium (Mg)	0 - 39,200	Clogging scale
Manganese (Mn)	0 - 2,000	May precipitate on oxidation
Mercury (Hg)	0 - 10	
Molybdenum (Mo)	0.029- 0.074	
Nickel (Ni)	0.005 - 2	
Nitrate (NO_3)	0 - 35	Drinking standard, 45 ppm
Nitrite (NO_2)	0 - 1	Organic pollutant
Oxygen (O_2, dissolved)	0 - 10	Corrosion-related
Phosphate (PO_4)	0 - 0.3	Eutrophication agent
(HPO_4)	0.75 - 2.05	
(H_2PO_4)	0.02 - 0.22	
Potassium (K)	0.6 - 29,900	Scale-corrosion accelerator
Rubidium (Rb)	0 - 169	
Silica (SiO_2, total)	3 - 1,441	Major scale constituent, corrosion inhibitor
Silver (Ag)	0 - 2	Mandatory limit; 0.05 ppm
Sodium (Na)	2 - 79,800	Scale-corrosion accelerator
Strontium (Sr)	0.133 - 2,000	
Sulfate (SO_4)	0 - 84,000	Clogging scale

Chemical Composition of Geothermal Waters, cont'd.

Constituent	Concentration in ppm	Comments
Sulfur (S)	0 - 30	
Total Dissolved Salts	47 - 387,500	
Zinc (Zn)	0.004 - 970	Toxic to fish if >0.3 ppm
Zirconium (Zr)	24	

The following are trace elements found at Sinclair #4 well, Salton Sea, California (Lit. 27):

Antimony (Sb), Beryllium (Be), Bismuth (Bi), Cerium (Ce), Dysprosium (Dy), Erbium (Er), Europium (Eu), Gadolinium (Gd), Gallium (Ga), Gold (Au), Hafnium (Hf), Holmium (Ho), Indium (In), Iridium (Ir), Liutetium (Lu), Neodymium (Nd), Niobium (Nb), Osmium (Os), Palladium (Pd),Platinum (Pt), Praseodymium (Pr), Rhenium (Re), Rhodium (Rh), Ruthenium (Ru), Samarium (Sm), Scandium (Sc), Selenium (Se), Tantalum (Ta), Tellurium (Te), Terbium (Tb), Thallium (Tl), Thorium (Th), Thulium (Tm), Titanium (Ti), Tungsten (W), Uranium (U), Vanadium (V), Ytterbium (Yb), Yttrium (Y).

TABLE 2

GAS COMPOSITION OF GEOTHERMAL VAPORS

Constituent	Concentration in volume percent	Remarks
Ammonia (NH_3)	0 - 5.36%	Noxious gas
Argon (Ar)	0 - 6.3	Minor inert gas
Arsenic (As)	0.002 - 0.05	
Boric Acid (H_3BO_3)	0 - 0.45	
Carbon Dioxide (CO_2)	0 - 99	Scale formation
Carbon Monoxide (CO)	0 - 3	Health hazard
Helium (He)	0 - 0.3	
Hydrocarbon C_2 and greater	0 - 18.3	
Hydrogen (H_2)	0 - 39	
Hydrogen Fluoride (HF)	0.00002	
Hydrogen Sulfide (H_2S)	0 - 42	Noxious gas, environmental Hazard, corrosion agent
($H_2 + H_2S$)	0.2 - 6	
Mercury (Hg)	0.007 - 40.7 (ppb)	Health hazard
Methane (CH_4)	0 - 99.8	
Nitrogen (N_2)	0 - 97.1	Major inert gas
(N_2 + Ar)	0.6 - 96.2	
Oxygen (O_2)	0 - 64	
Sulfide Oxide (SO_2)	0 - 31	Corrosion agent

TABLE 3

RELATIVE ABUNDANCE OF CHEMICAL COMPOSITION IN GEOTHERMAL WATERS

Major Constituents (maximum> 10,000ppm)	Secondary Constituents (maximum>1,000ppm)	Minor Constituents (maximum>1ppm)	Trace Constituents (generally<0.01ppm)	
Chloride	Aluminum	Arsenic	Antimony	Platinum
Sulfate	Iron	Barium	Beryllium	Praseodymium
Sodium	Bromide	Cadmium	Bismuth	Rhenium
Calcium	Manganese	Cesium	Cerium	Rhodium
Magnesium	Strontium	Copper	Dysprosium	Ruthenium
Potassium	Carbonate	Fluoride	Erbium	Samarium
Bicarbonate	Silica (total)	Hydrogen Suflide(total)	Europium	Scandium
	Ammonium	Iodide	Gadolinium	Selenium
	Boron	Lanthanum	Gallium	Tantalum
		Lead	Germanium	Tellurium
		Lithium	Gold	Terbium
		Mercury	Hafnium	Thallium
		Nickel	Holmium	Thorium
		Nitrate	Indium	Thulium
		Phosphate(total)	Iridium	Titanium
		Rubidium	Liutetium	Tungsten
		Silver	Molybdenum	Uranium
		Zinc	Neodymium	Vanadium
		Zirconium	Niobium	Ytterbium
			Osmium	Yttrium
			Palladium	

With reliable data, chemical composition of geothermal effluents can provide much useful information about the reservoir since the kinds and amounts of constituents depend on the reservoir environment: formation lithology, rock-water interaction, rock mineral chemical equilibria as well as pressure and temperature. The major environmental concerns in a geothermal system are the presence of noxious constituents in the effluent, corrosion and scale-formation in pipes. Corrosion in casing and surface plumbing may cause contamination of the environment by geothermal fluid; scale formation may make disposal of spent geothermal effluent difficult, and creates a solid waste disposal problem. Chloride, oxygen, pH and sulfide are the major constituents in geothermal effluent responsible for corrosion and calcite scale formation. Silica, sulfide and hydroxide are the other causes of scaling. Corrosion and scaling being chemical processes, not only the chemical composition but also other thermodynamic factors such as temperature and pressure will play a role in determining the nature and extent of corrosion and scaling.

It is of interest to compare the chemistry of geothermal waters with other types of waters. Figure 1 compares the ranges of major chemical constituents in geothermal water and in potable water. In general, the reported maximum concentrations of dissolved constituents in geothermal water exceed those in potable water. The situation is similar when geothermal water is compared with drinking, irrigating, feeding or sea water (see Tables 4 and 5).

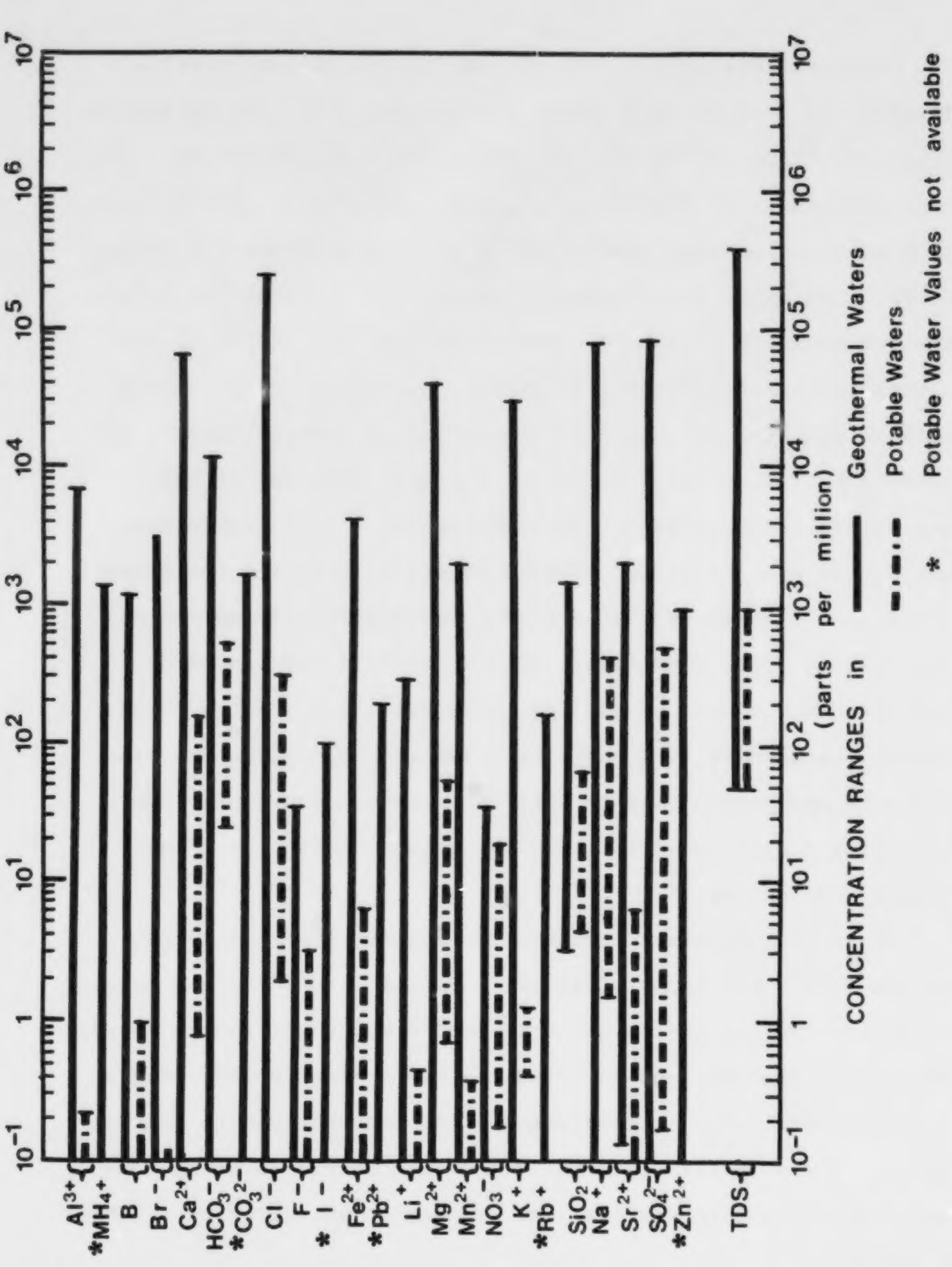

Figure 1. Chemical concentration ranges in geothermal and potable waters

TABLE 4

COMPARISON OF DRINKING, IRRIGATING, FEEDING AND GEOTHERMAL WATERS

Substance	Drinking Water (ppm) Recommended	Drinking Water (ppm) Mandatory	Irrigating Water (ppm) Threshold	Irrigating Water (ppm) Limiting	Feeding Water (ppm) Threshold	Feeding Water (ppm) Limiting	Geothermal Water (ppm) Range
Arsenic	0.01	0.05	1.0	5.0	1	-	0- 12
Barium	-	1.0	-	-	-	-	0- 250
Bicarbonate	-	-	-	-	500	500	0-10,000
Boron	-	-	0.5	2	-	-	0- 1200
Cadmium	-	0.01	-	-	5	-	0- 1
Calcium	-	-	-	-	500	1000	0-63,000
Chloride	250	-	100	350	1500	3000	0-240,000
Copper	1.0	-	0.1	1.0	-	-	0- 10
Fluoride	1.7	2.2	-	-	1	6	0- 35
Iron	0.3	-	-	-	-	-	0- 4200
Lead	-	0.05	-	-	-	-	0- 200
Magnesium	-	-	-	-	250	500	0-39,000
Manganese	0.05	-	-	-	-	-	0- 2000
Nitrate	45	-	-	-	200	400	0- 35
Selenium	-	0.01	-	-	-	-	trace
Silver	-	0.05	-	-	-	-	0- 2
Sodium	-	-	-	-	1000	2000	0-80,000
Sulfate	250	-	200	1000	500	1000	0-84,000
Zinc	5	-	-	-	-	-	0- 970
TDS	500	-	500	1500	2500	5000	0-390,000

TABLE 5

COMPARISON OF SEA WATER WITH GEOTHERMAL WATER

Substance	Typical Sea Water (ppm)	Geothermal Water Range (ppm)
Ammonium NH_4	0.05	0 --- 1,400
Arsenic As	0.02	0 ----- 12
Barium Ba	0.05	0 ----- 250
Boron B	4.6	0 ----- 1,200
Bromide Br	65	0.1 --- 3,080
Calcium Ca	400	0 ---- 62,900
Chloride Cl	19,000	0 --- 241,000
Carbonate CO_3	140	0 ---- 1,653
Fluoride F	1.4	0 ---- 35
Hydrogen Sulfide H_2S	60	0.2 ---- 74
Iron Fe	0.02	0 ----- 4,200
Magnesium Mg	1,270	0 ---- 39,200
Nitrate NO_3	0.7	0 ---- 35
Potassium K	380	0.6 -- 29,900
Silica SiO_2	7	3 ---- 1,441
Strontium Sr	13	0.133 - 2,000
Sodium Na	10,600	2 ---- 79,800
Sulfate SO_4	2,650	0 ---- 84,000
TDS	34,500	0 --- 390,000

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ABSTRACT

DEVELOPMENT OF GEOTHERMAL GAS SAMPLING EQUIPMENT

F. B. Tonani
GeoChemex, Berkeley, California

This paper summarizes the experience of the author in developing equipment for geothermal gas sampling under a wide range of conditions. Considered conditions have been: weight; ruggedness for operation in tough access sites by one or two man parties; capability to sample tiny seepages of gas from loose ground, scoriae, fissures, hand-drilled holes in fumarole areas; and independence from assumptions regarding what happens to a gas sample on storage (for example, no "air corrected" analyses).

These requirements have led to the development of small sampling tubes pressurized with gas carrier (the same to be used on GC analysis), then pressurized with the sample gas. Tubes are rugged and mailable to the laboratory even from far away countries in a matter of days. The accompanying gear is devised to allow careful aspiration of a small amount of sample that will not disrupt the naturally occurring stream. The apparatus allows not an abrupt sucking-in of uncontrolled amounts of gases, just what the specific hole, or fissure can supply without trivial contamination by the surrounding air. Glass syringes with Luer Lock have been the final choice, in spite of their fragility. But, plastic syringes are handy whenever usable. Standard items for GC have been tried and, in some cases, adjusted for custom use. Large volumes of sample can be safely handled in sampling tubes equipped with new Teflon-stem valves, to which neoprene O-rings have been added for better security on long term transport and storage.

Successful use of the Draeger detector tubes to analyze geothermal and volcanic gases in the field has been made possible by accurate study of their behavior. Questions, such as which components work under certain conditions, how to proceed under conditions entirely different from the ones envisioned by the manufacturer, etc. have been answered after years of only partially successful field missions. Water, carbon dioxide, hydrogen sulfide and H_2S+SO_2 tubes have proved to be dependable. For more precision at high concentration of carbon dioxide, pocket sized absorbing devices have been built. Commercially available materials have often needed to be complemented by specially-designed ones.

INTRODUCTION

The present paper summarizes the concepts that stem from the author's own experience in developing equipment for sampling geothermal gases. That experience has been mainly related to large scale geothermal exploration and to volcanic surveillance projects. Many aspects of it are relevant to the protection of environment and to the preparation of regulations, namely the assessment of natural discharges and the prediction of reservoir chemistry, i.e., of expected effluents on exploitation, at the very early stages in the development of the resource.

In fact, geothermal effluents are special in this respect. Many other industrial effluents are plainly man made. Others, e.g., tailings and effluents from mining operations, are not strictly man made, however, the rate at which they are released to the surface environment is much faster than under natural conditions.

One cannot be as positive about the fact that geothermal effluents are, in the essential, a net addition to the environment. Under certain plausible models of a geothermal field, a geothermal power plant might be just diverting essentially the same flow that takes place under natural conditions, rather than generating new discharge, and it is fair to say that actual conditions are likely to be intermediate. It is a matter of fact that thermal manifestations disappear as a consequence of harnessing geothermal energy in the same general area, and we know that many other unapparent manifestations were probably there and died off as well. Furthermore, the commonly held view that geothermal production is just tapping from a static storage of energy and carrier fluid is very questionable. Many volcanic and geothermal "systems" discharge to the surface energy and chemicals at a rate that compares well with what takes place during full-scale production of geothermal energy.

Therefore, the rate and distribution of flow of energy and chemicals under natural conditions as well as in production must be evaluated in order to assess the impact of geothermal development on the environment. Even in cases where the natural output does not greatly affect the final results, predicting reservoir chemistry and therefore the expected effluents is of much use in making decisions as to whether or not development is advisable and how development should be pursued, before substantial investments are made.

It is worth noting that the overall geochemical surveys, necessary to achieve the goals outlined here above, include first of all much water sampling and analysis. The reason for bringing gas sampling alone to the foreground in the present paper is that the state of the art in the latter domain seems far less satisfactory than in the former one. Actually, the gas sampling and analysis procedures that are mentioned here in connection with the described equipment are closely related to water study. For example, part of the interest in small samples stems from the significance of dissolved gas studies in the overall picture.

CONSTRAINTS ON THE DESIGN OF GEOCHEMICAL EQUIPMENT

Constraints on design of geochemical equipment fall in two broad categories, analysis specifications and constraints related to the working environment. Analysis specs include precision (also termed repeatability), accuracy, dependability and cost in as much as it is related to these specs. Constraints related to the working environment include other sources of cost, e.g. allowed capital investment, ruggedness, and more generally, the usability under actual field conditions.

There is great variety in specifications and other constraints. Regarding geothermal effluents, for example, determining whether discharge from geothermal power plants meets regulations requires that the analytical procedure be strictly repeatable in the first place, in order to provide certitude in judgment. That two observers come up with comparable results is more important, from the standpoint of implementing regulations, than having the obtained figures actually represent what they are said to represent chemically. The legally recognized procedure itself constitutes sort of an operational definition of the measured quantity.

This is not to say that we are not interested in actual composition, however, there is little doubt that this last knowledge does not need to be as unique and formally precise as the knowledge of whether or not a specific effluent meets any specific regulation. Knowing where, when, to what extent, and under which form some given chemical will interact with man is actually more important than just knowing its concentration in effluents. In other words, exact quantification of one figure at one specific point is usually less meaningful than some broad prediction of what the figure will be at a number of places and under various circumstances. The same consideration applies to predicting reservoir chemistry of the substances of interest prior to development, which is the main subject of the present expose'.

In all these cases, accuracy is definitely more relevant than sheer repeatability, behavior of the technique with different matrixes as opposed to behavior with one specific effluent is of concern, a capability to obtain more data at the expenses of precision and accuracy may be worthwhile, in as much as it upgrades the overall information obtained, and so forth. Therefore, the required analytical specifications may be quite different in connection with studying natural "systems" from what they are in monitoring industrial effluents of one specific nature.

Also, the constraints imposed by the working environment during early stages of exploration and development may be quite different from constraints effective after development of the resource. To begin with, in the former case economic constraints correspond to the high risk typical for early stages of development, as opposed to the economics involved in developing an established resource. Secondly, exploration is likely to take place far away from laboratory and other facilities, and quite possibly in rough country. By its very nature, exploration projects typically do not allow for long-lasting studies, and as a result, there is little question of time-series studies and of using permanent or semi-permanent field installations.

Of course, with progress, development conditions become closer and closer to ordinary conditions in an industrial environment. Here is a rough list of factors that have actually played a part in developing the materials described in this paper. The equipment ought to be operated by one man only, although usually with one helper. It should be possible to operate under various conditions, wind, dust and possibly rain. At the same time, basically the same equipment should cover the needs of different projects presenting very different field conditions. In fact, even in the same project diverse occurrences of gas have to be studied, which are usually hardly known at the onset.

Thus, a compromise must be reached between conflicting requirements, the equipment has to be flexible in its application, ensure reasonable accuracy, and remain small-sized, light and rugged as far as possible. Basically, it appears that the presently described equipment as well as some of the equipment reported in the literature has been designed to approach the characteristics outlined above at the expense of making it fool-proof and good for use by unskilled personnel. This is not a real loss in the case of early studies, because a great deal of decision making is left to field personnel, with regard to field analysis and the detailed implementation of sampling programs, so that skilled personnel are needed anyhow.

GAS SAMPLE CONTAINERS

DESCRIPTIONS

Two types of gas sample containers are currently utilized with capacity of 15 ml and 50 to 100 ml respectively. The former type (Figure 1) has two silicone rubber stoppers, is U-shaped, and includes a metal strap, spring and frame assembly to keep the stoppers in proper place. The second type is a regular gas sampling tube except for the valves, as 'torion' valves manufactured by Sovirel are utilized instead of whole-glass stopcocks. (Figure 2) The latter type looks very similar to that recommended by Giggenbach.[1]

Both tubes could be evacuated for gas collection, but practical use in exploration seems more dependable if they are pressurized above normal atmospheric pressure.[2] The former type is especially rugged and mailable, that is, it can reach the laboratory in shorter time than larger and less rugged items. Both types are safer than most other types vis-a-vis accidental leaks through valves.

DISCUSSION

Storage time is an important factor because the longer the storage time, the more probable, i.e., statistically more frequent become failures for a given container. There is no 'best' container in the absolute sense, as odds for failure depend on the way variable external action affects the container. Moreover, frequency of failures is only one factor, which must be weighed against other factors such as cost, handiness in field use and in transportation, and so forth. Neither the weight to be attributed to each factor nor the associated odds for failure with each factor are uniquely determined in the actuality.

The sample containers described in Figure 1 and 2 appear to be suitable in the environment prevailing in exploration projects and in the associated early evaluation of pollutants.

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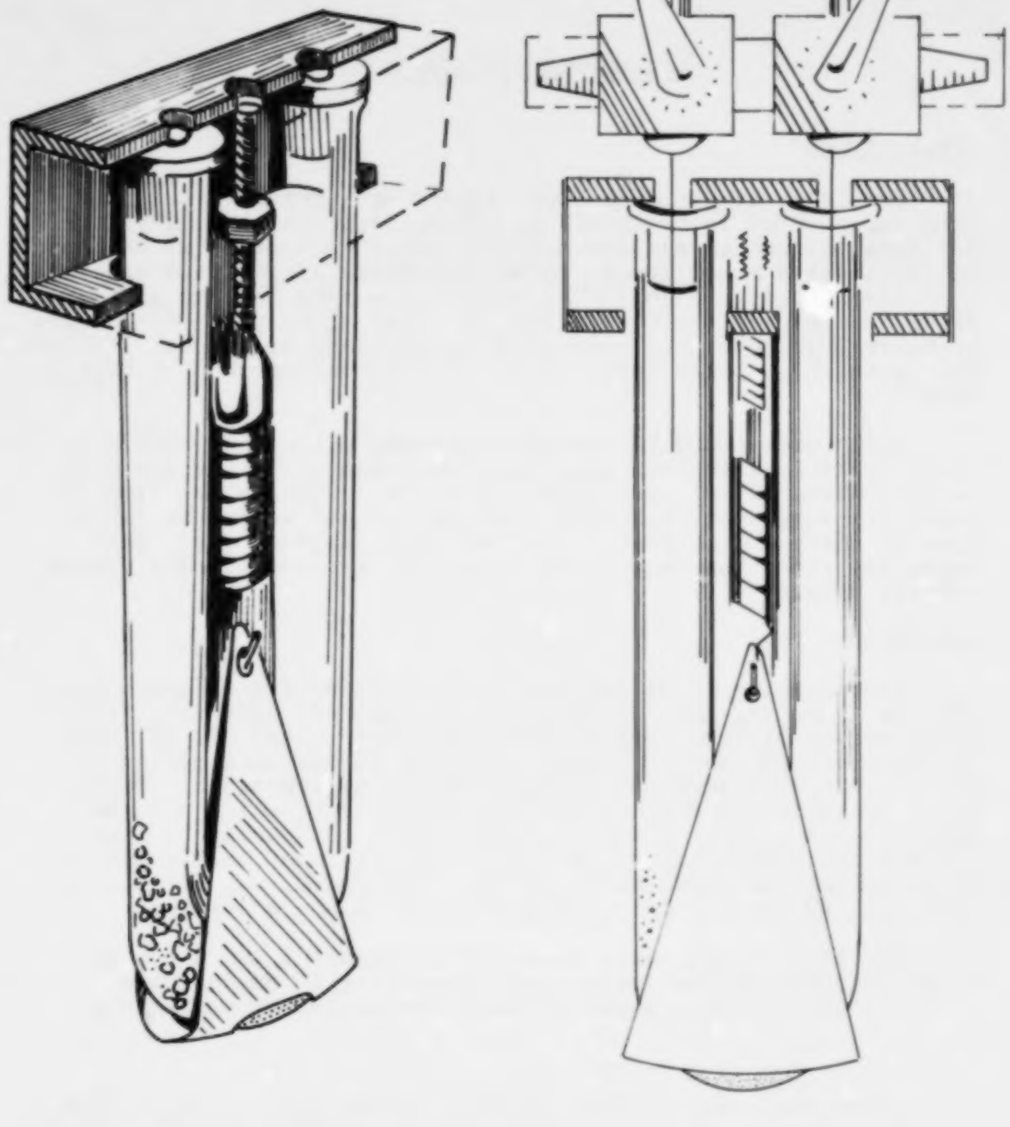

Figure 1.

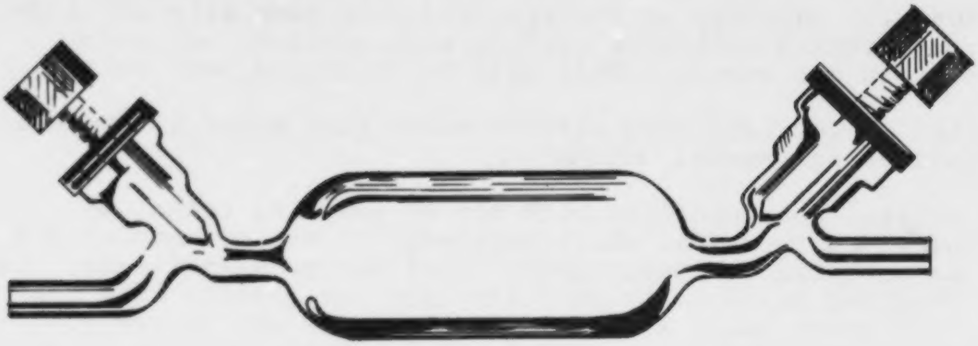

Figure 2.

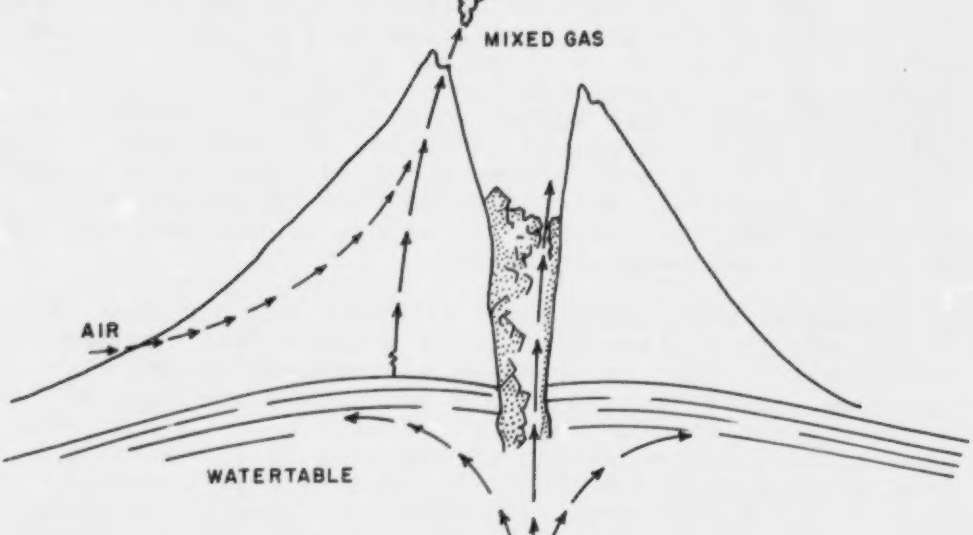
MIXED GAS
AIR
WATERTABLE
GAS

Figure 3.

In many cases one will have to collect more than one sample for different determinations if a broad range of determinations is required. This is just to cope with, (a) difficulties in collection, (b) behavior in storage, and more generally (c) a deliberate overall policy to operate with smaller aliquots rather than one sample. This will be discussed here below.

Let us consider some circumstances that point to the need for collecting several aliquots.

1. Trivial contamination with air on sampling cannot be afforded in cases, where knowledge of one or more of the atmospheric component gases is or may be significant. The required precautions on collection are usually such that collecting small samples is much easier and in certain cases the only feasible procedure. Trace amounts of non atmospheric gases are not affected by contamination by air, however, a larger volume of sample may be necessary. As a consequence, both one small and one large sample are required in such cases.

2. Pyrex containers are not safe for samples where helium must be determined. These samples are better stored in metal containers, and the converse applies for hydrogen sulfide. If the ratio between such sulfur gases as hydrogen sulfide and sulfur dioxide must be evaluated, or if hydrogen sulfide must be determined in samples containing oxygen, separation on sampling is the only safe procedure. In addition to classical but cumbersome procedures such as 'fixing' hydrogen sulfide in one sample, and determining total sulfur in the other, separation on molecular sieve 5 A proved effective for long term storage prior to elution and determination (Elskens et al., 1964). For such techniques which require packing the container with some material, sample containers of the sort described in Figure 1 are more convenient.

3. In a general way, using more aliquots has a number of advantages in respect to factors which affect samples erratically. Loss or breakage in transportation, mislabeling, heavy leak-in of air constitute one type of erratic event that we may term 'failures'. On the other hand trivial contamination in sampling or a basically undetectable leak are the other type of erratic event that we may term 'sampling errors'. Duplicate sampling is an effective protection vis-a-vis erratic events provided the probability of occurrence of such an event is not too great. One may require different levels of safety depending on project features, but multiple sampling is

cost-effective, provided the expected cost of failure exceeds the cost of additional sampling tubes and time. Typically for the environment of exploration, i.e., for early assessment of new areas, double-sampling is expected to result in 2-10% increase in sampling cost. For the expected saving on failures to exceed the cost of double-sampling the following conditions must be fulfilled;

P(1-P) greater or equal 0.1-0.02

respectively, where P is the probability of failures. Double-sampling is seen to be cost-effective if P exceeds 10-2% respectively. Similarly, 20-4% failure would cost-justify triple sampling.

It is worth drawing attention to the fact that the reasoning above holds for a given equipment, that is, for a given P value, whereas it is of no help by itself in selecting the most appropriate container. However, containers for small samples and an adequate sampling outfit reduce the average cost of multiple sampling and are preferable in this respect. Basically, the overall cost of extensive sampling in new and/or remote areas is comparatively large, and both costly equipment of the type described here and multiple sampling are cost-justifiable in projects dealing with the assessment of the natural discharge.

FIELD GAS ANALYSIS

INTRODUCTION

Gas analysis in the field serves four main purposes:

1. It is possible to make relatively extensive gas surveys, that offer a picture of the overall pattern in scattered gas flow. In addition to directly supplying data, online field analysis allows for adjustments in the sampling pattern that result in better evaluation of the gas stream.

2. Time-series of analyses are more easily obtained by field analysis than by repeated sampling. Investigation of dependence on time is part of overall flow estimates, but also supplies information on different hydrodynamic components of the same stream. Figure 3 points to a typical situation where two different gas streams undergo mixing. The mixing ratio is affected by minute changes in external conditions. Time-series over a short time span are apt to

detect the corresponding changes in composition; they also reveal the existence of and assess the two hydrodynamic components.

3. Field determination offers a safe way around problems arising from sample storage. Sulfur gases are specially reactive and may be heavily affected by storage prior to analysis. Field determination may be preferable to 'fixing' hydrogen sulfide.

4. One problem with gas sampling is that you do not really see what you are handling, it is as if you were blindfolded. There are several ways of monitoring gas sampling by on-line analysis; this substantially improves the average quality of the samples obtained.

A great number of apparatus is available nowadays for field work in the broad sense, including gas-chromatographs, as well as infra-red, electrochemical and other analyzers. In connection with the early prediction of possible pollutants and the assessment of natural discharge prior to the development of geothermal resources, however, hydrogen sulfide and volatiles such as ammonia, mercury and arsenic are the major concern. Under the conditions prevailing before industrial development, preliminary evaluation and prediction of the discharge of such chemicals depends to a sizeable extent on water analyses. Surveying the mercury content in air might deserve consideration, however, it is not discussed here, as mercury determination in soil is likely to be a valid substitute for it.

The present expose' shall therefore concentrate on equipment related to the assessment of the major constituents of the gaseous discharge and hydrogen sulfide. However, the design of the equipment resulted also from concern with constituents significant in exploration, such as methane, hydrogen, etc. More specifically, some pocket-sized items portable by an individual even in rough country will be described. Such equipment is viewed essentially as an aid in sampling.

DETERMINATION OF CARBON DIOXIDE BY ABSORPTION ON NaOH

High concentrations of carbon dioxide occur frequently in geothermal manifestations and reservoirs. Direct measuring of in excess of 90% carbon dioxide requires a precision on reading of, say, better than 2% if significant data must be obtained. In the laboratory such high concentrations were determined by absorption on NaOH, e.g., by the Orsat's method. The idea is simply to measure the volume of the initial sample and then the volume of the residual, unabsorbed gas. In terms of percent error for carbon dioxide, if the residual volume is very small, the precision of the estimate of the absorbed volume is accordingly very good.

Actually, the sum of acid gases, CO_2, H_2S, and SO_2, is so determined. Typically in geothermal gases hydrogen sulfide is a few percent, or less, of the carbon dioxide content. Therefore, determining it separately and subtracting the result from the data obtained by absorption still leaves us with excellent precision on the estimate of carbon dioxide concentration. Figure 3 shows a small absorption apparatus for field use. Some 10 ml of 4 N NaOH are prepared in the field to fill up the measuring pipet, in which a ballast of air is left in order to keep the increase in pressure within 10% of ambient pressure. The sample is injected with a syringe, e.g., a plastic disposable syringe. Typically one or more shots of 10-ml sample can be made, and reading is from 0 to 0.50 ml with a precision better than 0.05, making it possible to check for purity of CO_2 + H_2S gases up to in excess of 99.99%, in principals.

As a reasonable precision of 10% can be maintained in sample additions down to 1 ml by using appropriate syringes, the lowest concentration of carbon dioxide still measurable with this device is as much as 50%. Thus, the pocket-sized absorbing pipet depicted in Figure 4 covers the concentration range of carbon dioxide from 50 to 99.99%. It is of great use in checking for proper sampling conditions on sampling high CO_2 gases, where even limited contamination of the sample by air is bound to completely distort the chemical composition of the gas.

DETECTOR TUBES

The principle of detector tubes goes back in time to the lead acetate paper for hydrogen sulfide, the Marsh method for arsenic, and in more recent times, the 'tupfel' techniques worked out by Feigl and others. Use of this technique in volcanic and geothermal environment has been discussed and described by Elskens, et al. (1964) and F. Tonani (1972). It consists of having a known amount of gas sample flow through the DT, so that the constituent to be determined in the sample reacts with the solid stationary phase, resulting in discoloration of the packing. The amount of discolored packing is proportional to the amount determined, and a visual reading can be made if some conditions are fulfilled. With uniform, plug-wise flow of

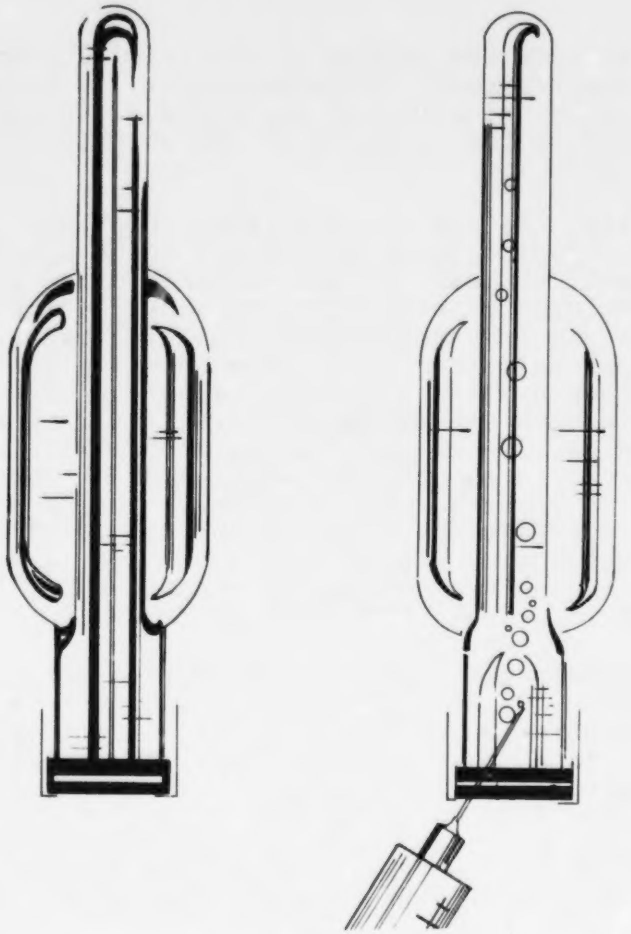

Figure 4.

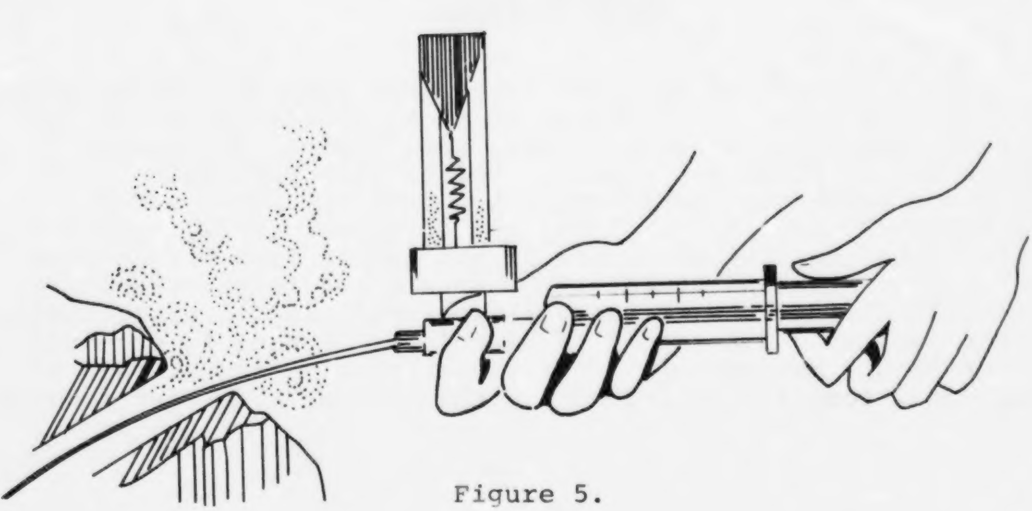

Figure 5.

the gas, as prerequisite to uniform, sharply outlined discolored zone, precision may be very good.

Techniques described by the manufacturers of DT are devised for monitoring air in regard to explosive or toxic gases and vapors. Therefore, they are designed for the low range of concentration and/or for using comparatively large volumes of sample. In analyzing geothermal gases, especially in doing it with a view to assessing significant amounts of such gases as carbon dioxide and hydrogen sulfide, the concentrations encountered are in the high range, and using small volumes of sample is often required. Therefore, a number of variations of the original technique had to be devised with the aim of obtaining accurate results under such diverse conditions.

Experience has indicated that detector tubes for water vapor, carbon dioxide, and hydrogen sulfide as well as H_2S + SO_2, are dependable for field use. Hydrogen sulfide DT are very handy and rugged. Sensitivity is sufficient for most practical purposes, being about 2 ppm for a 100-ml sample. For determination in air, e.g., on assessing total flow patterns, sensitivity is even better. The precision, 5-10%, is sufficient for the purpose indicated here, and accuracy is better than that obtained by analyzing samples after transportation and storage.

Carried or condensed water in the gas stream jeopardizes the DT and must be removed prior to analysis. The DT in itself, however, can work under high temperature and therefore could be used for superheated steam. For example hydrogen sulfide DT have been used at extremely high temperature at a volcanic vent on Mt. Etna, Sicily. Later cross-checks in the laboratory have indicated that the data are still dependable under such extreme conditions. The DT still works after complete dehydration, and in fact detects S_2 vapor in addition to H_2S under high temperature conditions.

H_2S + SO_2 tubes have iodine as a reagent and therefore cannot be operated at high temperature. They are used only for concentrations in the order of several percent units, by volume, which do not occur very often in samples from occurrences of mixed origin.

Carbon dioxide detecting tubes are now manufactured for a broad concentration range, including the 60% range. However, the more sensitive tubes in the series can be used up to the same high concentration level by just using lesser volume of sample and concurrently applying appropriate changes in the determination technique. These DT's are especially sensitive to heat and light. They 'age' faster than other DT's, therefore, the number of different types kept in stock should be as small as possible.

The reaction in the CO_2 DT is reversible and the discolored layer may 'travel' and spread on flushing the DT with a large volume of gas, resulting in erroneous readings. Thus, flushing a small sample into a CO_2 DT for determination requires some additional precautions besides the quantitative handling of the sample volume through the tube. Precision is 10% of read value and may be better under favorable conditions. Sulfur gases, and more generally reducing gases, interfere with this reaction, resulting in the 'fading away' of the discoloration. Fade color in CO_2 DT points to either the presence of some amount of sulfur gases, or over-aged DT. Hydrogen sulfide and sulfur dioxide can be removed in different ways, e.g., a short segment of an iodine DT (one DT can be cut into a number of such scrubbing-analyzing devices). A cotton-wool plug impregnated with iodine from a regular alcoholic iodine solution can be inserted into the inlet end of the DT and scrub all sulfur gases from the sample. Thus, DT's and the absorption device described earlier cover the range of concentration from less than atmospheric (300 ppm) to very pure carbon dioxide.

Water vapor is not of concern as a contaminant to the atmosphere, and its determination in naturally occurring geothermal gases serves different purposes. For example, the amount of water vapor in gas streaming out of natural steam vents indicates whether there was superheating of the gas stream by hot country rock. Mixing with air is also better understood on the basis of such data. Referring such gases as carbon dioxide, hydrogen sulfide, methane etc. to the companion amount of steam is of much use in interpreting the data in terms of vaporization from the water table, mixing with air in the overlying unsaturated zone and so forth.

As water vapor is quite often the overwhelming constituent in fumarole discharge, its determination in the surrounding air is very suitable in view of determining the total discharge into the atmosphere based on average composition and wind velocity. DT's in general are very suitable as integrating devices in such cases where the average composition must be determined. In the case of water and carbon dioxide, however, one has to be wary of the fact that both reactions are reversible and the discolored zone 'travels' along the DT. In the water tube, the absorption of water is reversible, but the discoloration is irreversible, therefore, much attention must be paid to controlling the gas flow through the DT. Expected precision is also about 5-10% if the DT is properly handled, e.g., to avoid condensation of water.

SAMPLING OUTFIT

The sampling outfit proper consists of devices which transfer the gas sample from the sampling point to a sample container or to a detecting device, e.g.,detector tubes. A number of devices are required to collect transferable samples from dissolved, bubbling or streaming gases (see for example Figure 6 showing an extraction device for dissolved gases). They are not discussed here; only the sample transfer outfit is presented. Under the constraints described earlier, the requirements put on such sample transfer outfits are pretty strict, as trouble in the middle of sampling under rough field conditions, in hardly accessible areas, may be very costly.

All in all, syringes fitted with hand operated valves are suitable and safe. For easier operation without giving up much in the way of safe results, a manifold consisting of two three-way valves such as depicted in Figure 1 has proved useful. Although similar 'plumbing' may be designed for use with other gas sampling tubes, it is apparent from Figure 1 that the U-shaped container makes an especially compact assembly possible, Figure 5 shows how a similar outfit can be operated by one person only, even in a difficult environment.

Syringes with automatic valves for operation as hand pumps are marketed by several manufacturers. Automatic valves, however, are subjected to getting stuck. For example, valves that operate satisfactorily with water or gas alone are troublesome when moisture or carried water reaches them and is retained by capillarity at the narrow sections of the valves.

Draeger supplies a hand pump for sampling through the detector tubes. One stroke is 100 ml and smaller amounts cannot be handled, which is very inconvenient in the analysis of geothermal gases by DT's. A hand pump marketed by Nalgene has favorable features. One stroke is only 14 ml, and it is fitted with a vacuum gauge. This allows for checking that the sample flows smoothly and completely into the sampling or analysis line. Moreover, a fraction of a stroke can be measured down to one milliliter by sticking a scale on the plunger shaft. Admixtures of water, however, appear to result in frequent breakdowns in that the pump is no longer tight. While battery powered pumps are of use when heavier and more sophisticated equipment is allowed, e.g., when sampling man made wells and other easily accessible settings, their use is not described in connection with the specific subject of this paper.

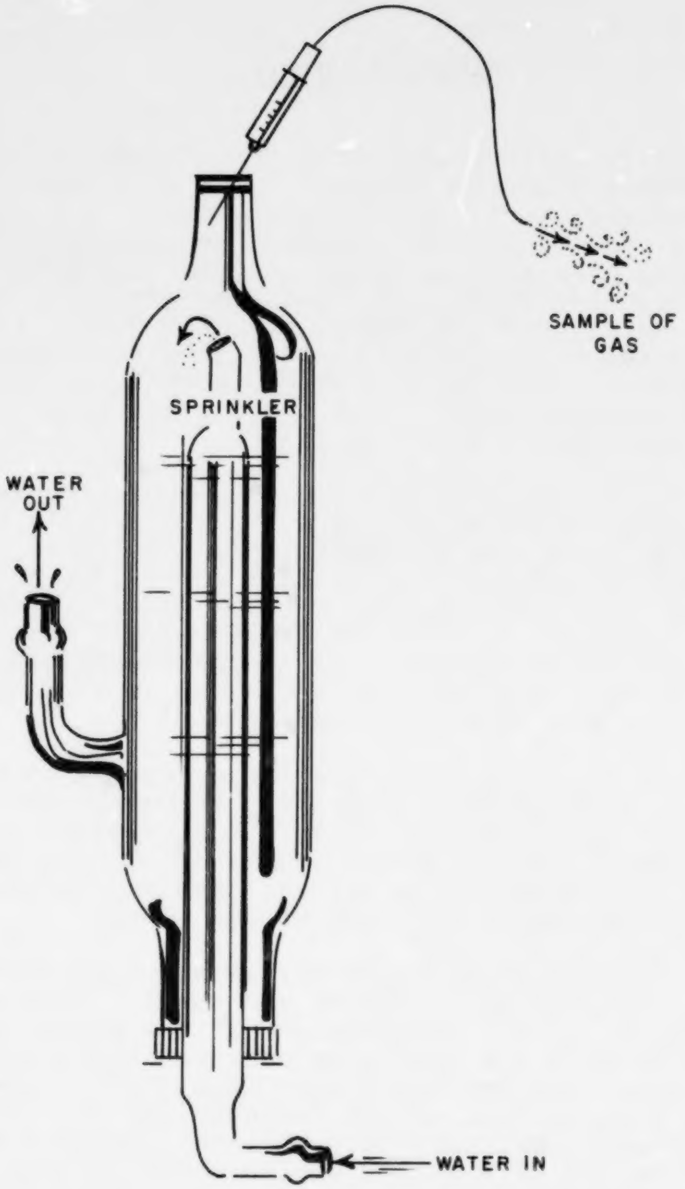
SAMPLE OF GAS
SPRINKLER
WATER OUT
WATER IN

Figure 6. Circulation by gravity, hand pump, or power pump

ABSTRACT

SAMPLING FOR RESERVOIR FLUID RECONSTRUCTION

M. J. Reed
U.S. Geological Survey, Menlo Park, California

Much can be learned about the geochemistry of a geothermal system if the chemical composition of the reservoir fluid is known. Downhole sampling methods used extensively by the New Zealanders provide the most accurate compositions of reservoir fluids. In the absence of a downhole sample, the fluid composition can be mathematically reconstructed from the chemical analyses and mass flow rates of separated gas and liquid phases sampled at the surface.

The major drawback of fluid reconstruction from surface samples occurs when several permeable strata or several fractures containing fluids of different compositions contribute to the well flow. In these cases the flow from the wellhead is a mixture of the reservoir fluids from the producing zone, and the reconstruction gives an average fluid composition. If a well produces from a single reservoir fluid, the reconstructed composition will be independent of the flow conditions; but, if a well produces a mixture of fluids, the composition will change as the flow conditions change.

At Cerro Prieto, Mexico, several wells produce from liquid-filled permeable strata or fractures over a large range of depth. Liquids of distinct chemical composition enter a well when the pressure in the well drops below the pressure in the permeable zone. At high flow rates, when the pressure in the well is low, all the permeable zones are able to contribute to the flow. Sampling a well at different flow conditions provides a general indication of the composition range in the reservoir fluids.

At The Geysers, California, some wells produce steam from fractures distributed over a large depth interval. Changes occur in the gas composition of the steam. In a single well, the concentrations of hydrogen sulfide and boric acid tend to be higher in shallow fractures than in deeper fractures. In this low-pressure system, the deliverability of the fractures appears to control the change in composition with changing flow conditions. Sampling at the wellhead under a variety of flow conditions will supply data on the chemical range of fluid in the reservoir fractures and allow the prediction of composition for any flow conditions.

Techniques of Pressure and Temperature Measurement and Sampling in Geothermal Wells

by Laurence W. Ross, Larry L. Brown and Ralph E. Williams

Denver Research Institute
University of Denver
Denver, Colorado 80208

Abstract

The Denver Research Institute, in the course of a program for establishing a manual for the design of wells for exploitation of hydrothermal sources of geothermal energy, developed a need for highly accurate temperature and pressure measurements, and for determining the chemical composition of the fluid deep within the well, before flashing took place. Therefore DRI reviewed the scientific principles available for performing such measurements, and designed a probe for T and P measurements in real time. This probe was tested for the first time in well 8-1 in the East Mesa field in September 1976. The sampler selected for high temperatures is based on a design that was developed at the Los Alamos Laboratories, but commercially available samplers can be used at temperatures up to about 400°F. Laboratory and field results, and a comparative review of measurement tools available to the geothermal industry, are reported. Experiences of other investigators, and current industry trends, are also summarized.

I. Introduction

The Denver Research Institute has the mission, under Contract EY-76-S-02-2729.*000 from the U.S. Energy Research and Development Administration (ERDA), to perform high-accuracy measurements of temperature, pressure and chemical composition deep within geothermal wells that are flowing in the two-phase mode. Such wells are often called "flashing" wells.

DRI has developed a tool for measuring pressure and temperature up to 2000 psia (135 atm) and 500°F (260°C), which should be useful in most of the two-phase wells and liquid dominated wells now in existence or contemplated. Sampling devices are available for extracting fluid samples up to 1 liter in volume from geothermal wells at these levels of pressure and temperature, but a simplified design involving the actuation of a solenoid valve is proposed.

II. Principles of Pressure and Temperature Measurement in Geothermal Wells

a) General considerations

Measurement of pressure or temperature involves the creation of an electrical or mechanical signal that is a known function of the measured effect.

Mechanical measurements within a geothermal well may be stored inside the measuring probe for later interpretation, but electrical measurements are relayed to the surface for "real-time" observation. Therefore electrical measurements depend on a transducer to transmit the fundamental electrical signal to signal-conditioning apparatus either within the probe or at the surface, to permit a reading at the surface. Common principles employed in transducers are listed in Table I, and discussion may be found

Table I

Types of Transducers
for Measurement of Pressure and Temperature

Electrical Parameter and Transducer Type	Typical Application
a) Passive Transducers	
1) Resistance	
Potentiometric type	Pressure, displacement
Strain gauge	Force, displacement
Hot wire meter	Gas pressure
Resistance thermometer	Temperature
2) Capacitance	
Variable capacitance gauge	Pressure, displacement
3) Inductance	
Magnetic circuit transducer	Pressure, displacement
Reluctance pickup	Pressure, displacement
Differential transformer	Pressure, displacement, force
Eddy current gauge	Displacement
Magnetostriction gauge	Pressure, force
b) Self-Generating Transducers	
Thermocouple, thermopile	Temperature
Piezoelectric pickup	Pressure changes

in modern textbooks, for example, that of Cooper.[1]

The majority of electrical measurement principles generate relatively weak signals which suffer in accuracy when transmitted over the length of a submerged cable, which may extend for three miles below the surface. This circumstance has led to a need for electronic assemblies that can be inserted into geothermal wells in order to achieve signal conditioning, or at least signal amplification, within the well. Progress in such "downhole electronics" is only now beginning to be observable, as discussed below.

b) Pressure measurements

The absolute pressure within geothermal wells may be sensed by one of three basic principles: piezometry, strain gauges, or bourdon techniques. All three are available in commercial packages, but they are subject to various limitations.

The most accurate method is probably the use of piezoelectric crystals. The Hewlett-Packard Company of Palo Alto, California, manufactures a pressure gauge for which a resolution of 0.01 psi is claimed up to a total pressure of 12,000 psi with no hysteresis and with high stability. The quartz crystal transducer is fabricated such that its resonant frequency shifts according to the applied pressure. The gauge requires the use of a single conductor cable. It has no moving parts, and it is fairly compact: 1-7/16 in. OD, 39-3/8 in. long, weight 11 lb. The most serious limitation of this gauge is the maximum temperature limit of 150°C imposed by the electronic elements inside the probe.[2]

Another very accurate system is the Sperry-Sun downhole concept, in which a gas (e.g., nitrogen) is supplied through a small tube to a chamber deep within the well, and the downhole pressure is balanced at the surface.[3]

The tube is 3/32 in. OD, stainless steel. This system is fundamentally the same as that reported by Fournier and Truesdell of the U.S. Geological Survey,[4] but the Sperry-Sun system incorporates an electronic system for data readout. Reports from field applications have indicated that the Sperry-Sun system is accurate to within 2 psi, and that it is limited to a depth of about 4,000 ft. because of the adverse effects of heat and salinity on the stainless steel tube. Another potential limitation is the chamber diameter of about 3½ in. OD which may present a significant obstacle to flow within the well.

Strain gauges are widely used in the geothermal industry because of their simplicity and flexibility, but their low electrical output (i.e., their low change in resistance as a function of applied pressure) generally limits their use to shallow applications where temperatures are sufficiently low to permit downhole electronics for amplification of the signal for transmission to the surface.

A purely mechanical device for pressure measurement is marketed by the Kuster Company of Long Beach, California. It features a bourdon element that drives a scribe, creating a trace on a brass foil, using a mechanical clock to move the scribe at a constant rate, thus creating a record of pressure vs. time. The foil is interpreted later under a magnifying assembly. The gauge is compact, but is suspended on a wire line that presents some risk of kinking or breaking when the flow is fairly rigorous, according to field experience.

The Denver Research Institute has a need for relatively high accuracy up to 250°C and 2000 psia, and this accuracy cannot be achieved with any of the principles discussed above, at the depths of interest (up to 2 miles). To achieve the desired accuracy, DRI has adopted the potentiometric type of transducer, because it is the only type that will provide a relatively high electrical voltage output without the necessity of downhole electronics. Four transducers were ordered from Gulton Industries in Costa Mesa, California, including two specially built transducers for measurement to 2000 psia at 250°C, and two stock transducers for measurement to 500 psia at 180°C. The transducers depend on a bourdon tube to drive a slide across a resistance winding; the winding is excited by a constant current, and the measurement is taken as the potential at the resistance according to the slide's position. The temperature characteristics of the Gulton transducers are fairly linear except at the most extreme conditions (Fig. 1).

The DRI transducers feature resistance windings with 330 turns of wire, so that the 2000 psia transducers will record pressure changes in steps of about

$$\frac{2000}{330} \cong 6 \text{ psi.}$$

This is not necessarily a disadvantage for absolute pressure measurements, since any measured "step" must occur at a pressure level where the slide has just encountered the next turn of the winding, and the value of the resistance (and therefore the pressure) at this particular point is known within fairly high precision, e.g., 2 to 3 psi. However, the usefulness of these transducers for recording pressure fluctuations is still not well understood, and field tests in geothermal wells are needed to resolve this question.

c) Temperature measurements

Measurement of temperature in geothermal wells is simpler than measurement of pressure, because no mechanical force or displacement is involved.

Thermistors are widely used for temperature measurement in geothermal

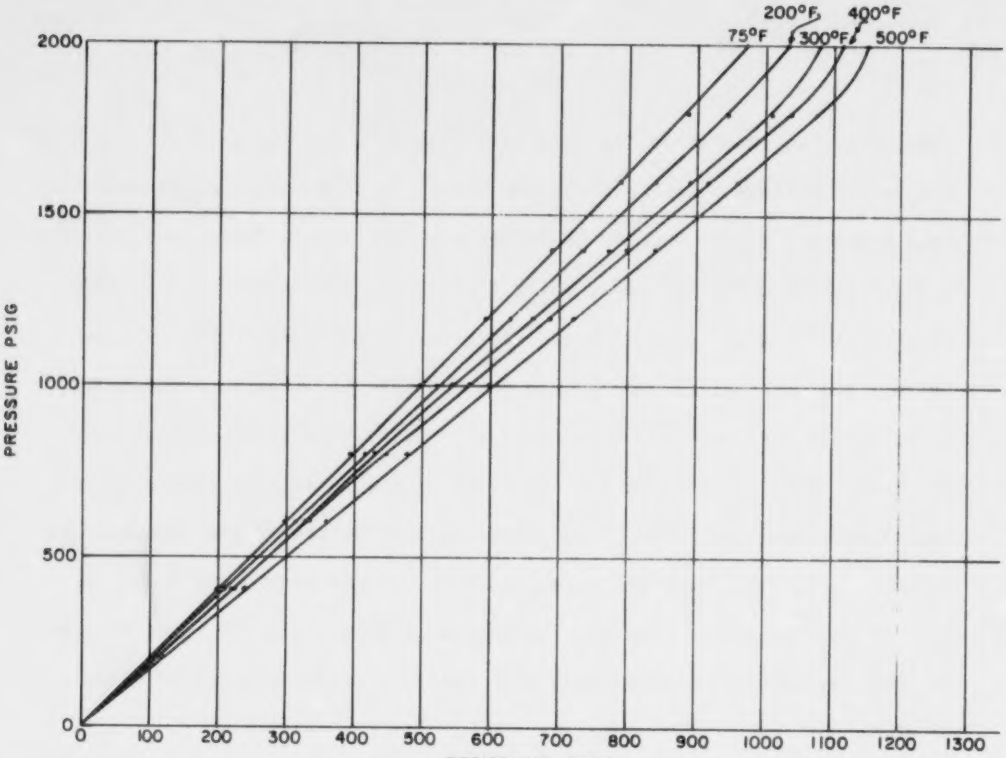

Figure 1. Pressure and temperature characteristics of one of the 0-2000 psia pressure transducers used in the DRI probe

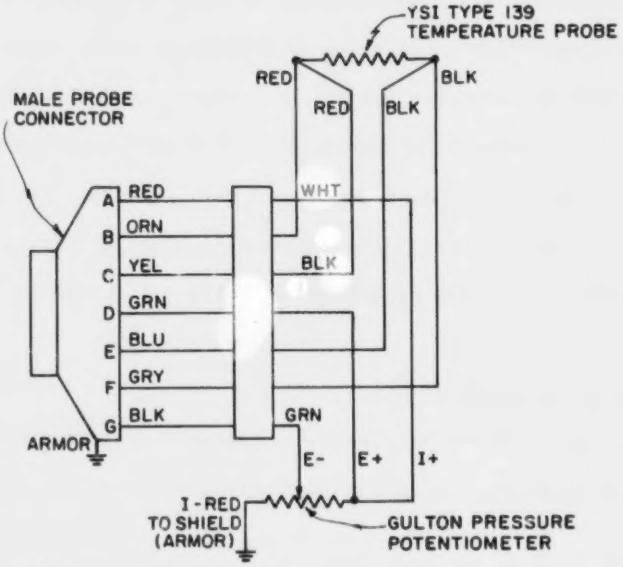
YSI TYPE 139
TEMPERATURE PROBE
RED
BLK
RED
BLK
MALE PROBE
CONNECTOR
A
B
C
D
E
F
G
RED
ORN
YEL
GRN
BLU
GRY
BLK
WHT
BLK
GRN
ARMOR
E-
E+
I+
I-RED
TO SHIELD
(ARMOR)
GULTON PRESSURE
POTENTIOMETER

Figure 2. Wiring diagram of the pressure and temperature sensing elements used in the DRI probe

wells, but DRI has elected to use a platinum resistance thermometer because it can be purchased off-the-shelf at a guaranteed accuracy well within 1°F. The electrical circuitry associated with the platinum resistance thermometer is integrated with the wiring for the pressure transducer as shown in Fig. 2, such that both employ the armor of a seven-conductor cable as ground.

Thermocouples can be used for downhole temperature measurement, if a thermopile can be assembled that is sufficient to create an electrical signal that can be measured accurately at the surface, and if its reference junction can be held at a cold temperature for a sufficient time. This is the technique used by the Los Alamos Laboratory.

A mechanical gauge for temperature measurement is available from the Kuster Company (see II.b above), and it can be used in combination with the Kuster pressure gauge to obtain a P and T log simultaneously.

III. Sampling of Fluids in Geothermal Wells

a) General considerations

Sampling of geothermal fluids is generally achieved at the wellhead. In the case of two-phase flow (i.e., flashing flow), which will be the most prevalent case in wells intended for electrical power production, this means that both a vapor phase and a liquid phase must be sampled and analyzed. Furthermore, both flow rates must be known accurately.

Sampling at the wellhead introduces errors due to uncertainties in chemical analysis and flow rates, and this is especially true for gases such as CO_2, H_2S and NH_3 which are distributed between the vapor and liquid phases of the fluid.

This situation has led the Denver Research Institute to seek a sampling concept which could be employed deep within producing geothermal wells, at depths where the vapor phase has not yet developed in the flowing fluid.

Several sampling devices suitable for use in geothermal wells are available, including at least two that are commercially manufactured.

Sampling devices that operate on mechanical principles have been employed for many years, but only the Kuster design (Kuster Company, Long Beach, California) and the Klyen design (Forgan Jones Limited, Auckland, New Zealand)[5] are presently available for purchase. All mechanically actuated samplers rely upon a force applied at a given time in order to open (or close) a valve port. Either a check valve prevents the incoming sample from reversing direction or, in the case of the "flow-through" principle of sampling, closing of a valve trips the sample in a chamber.

Electrically actuated samplers are available from the oil well service industries, but they feature a maximum temperature limit of about 300°F.

The Los Alamos Laboratory has developed a double-chamber sampler for extraction of liquid samples within geothermal wells at temperatures up to 200°C. Two chambers, each approximately 250 ml in volume, can be opened sequentially (before-and-after) by actuation of a drive motor.

The Denver Research Institute has proposed a sampling concept based upon actuation of a solenoid valve, for use of temperatures up to 250°C. A representative design is shown in Fig. 3. The solenoid valve is actuated at the surface at the desired time, admitting fluid into the evacuated chamber at left; a check valve retains the sample in the chamber, as in other sampler designs (see above). Extraction of the sample for analysis involves a certain degree of design and technique, depending on the measured

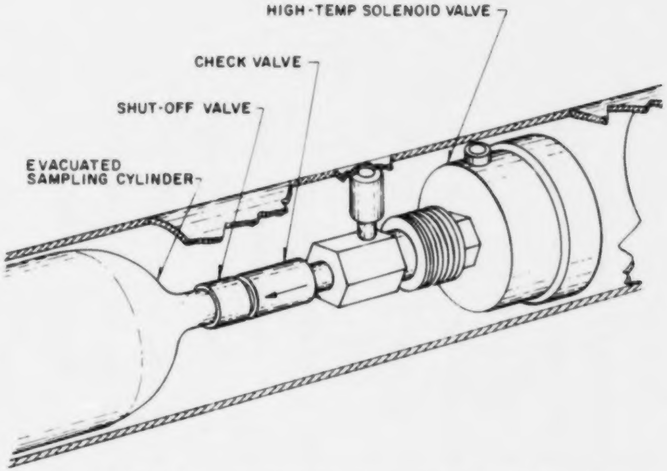
HIGH-TEMP SOLENOID VALVE
CHECK VALVE
SHUT-OFF VALVE
EVACUATED SAMPLING CYLINDER

Figure 3. Proposed high-temperature solenoid valve-actuated sampling system

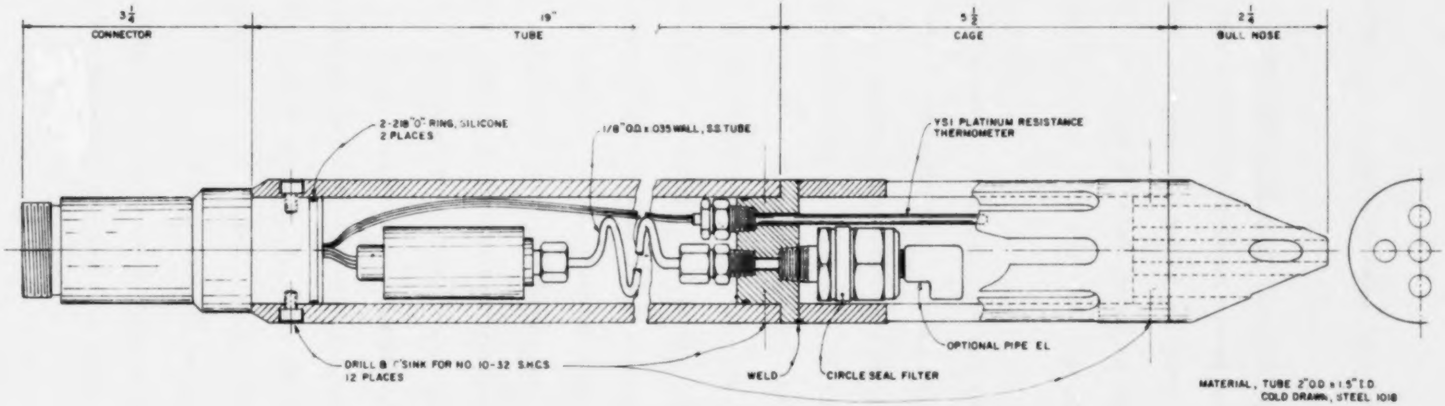
3 1/4
CONNECTOR
19"
TUBE
5 1/2
CAGE
2 1/4
BULL NOSE
2-218 "O" RING, SILICONE
2 PLACES
1/8" O.D. x .035 WALL, SS TUBE
YSI PLATINUM RESISTANCE THERMOMETER
OPTIONAL PIPE EL
DRILL & C'SINK FOR NO 10-32 S.H.C.S.
12 PLACES
WELD
CIRCLE SEAL FILTER
MATERIAL, TUBE 2" O.D. x 1.5" I.D.
COLD DRAWN, STEEL 1018

Figure 4. Schematic diagram of the DRI probe for measuring pressure and temperature in geothermal wells

quantities of interest,and their relative importance.

IV. Field Experiences in Measurement

The Denver Research Institute visited the East Mesa geothermal field in the Imperial Valley in September 1976 in order to perform the first in a series of three tests in geothermal wells as required by Contract EY-76-S-02-2729.*000 with the U.S. Energy Research and Development Administration (ERDA)

DRI has constructed a probe to house the pressure and temperature measuring capabilities described in Section II above. The probe is designed to contain the measuring elements in a body of 2 in OD. The probe is shown schematically in Fig. 4. It is about 30 in. long, including the cable head connector for connection to a seven-conductor armored cable. The probe is shown ready for application in Fig. 5.

DRI has also constructed a calibration assembly for testing of the pressure and temperature sensors under laboratory or field conditions. The calibrator is designed for testing up to 3000 psia and 600°F, and it measures 3 in. ID and 48 in. interior length. A dead weight test assembly provides the calibration pressure, and temperature adjustment is provided by electrical heater windings and a West model 400 controller. The field-ready calibrator assembly is shown in Fig. 6.

The U.S. Geological Survey provided the field support for application of the DRI probe at the East Mesa field in September 1976. Measurements were performed in well 8-1 of the East Mesa field. Figure 7 shows the operation of erection of the riser pipe (6 in. diameter) which is designed to contain the probe and the attached sinker bars, and it also shows the U.S.G.S. logging truck which provides the cable, winch and electronic measurement capability

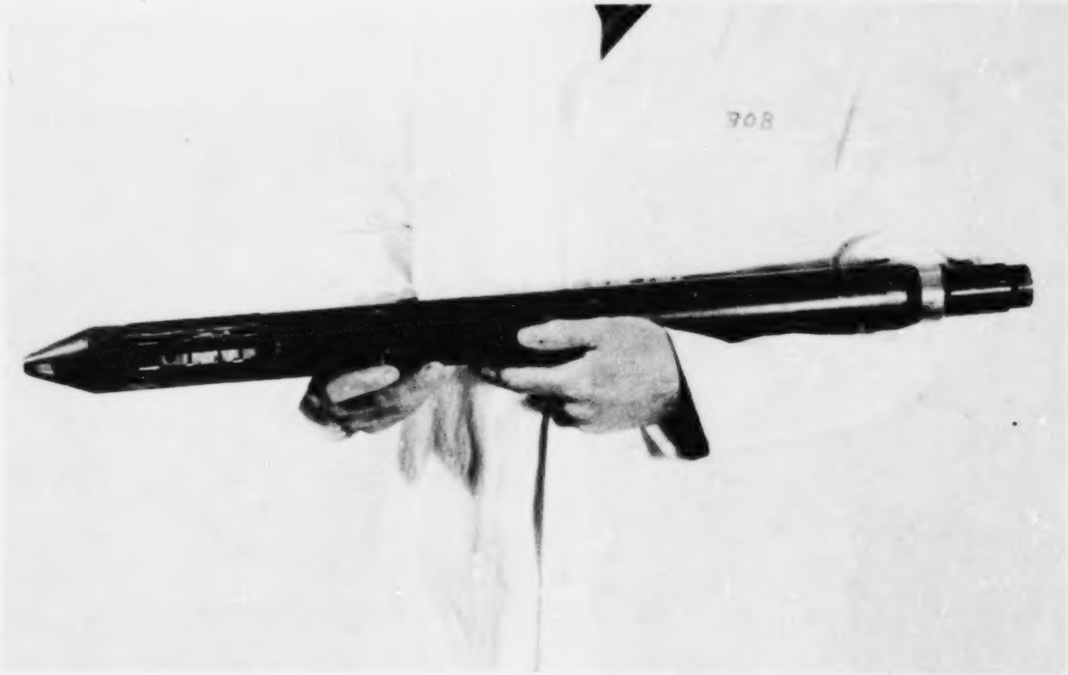

Figure 5. The DRI probe, assembled and ready for use.

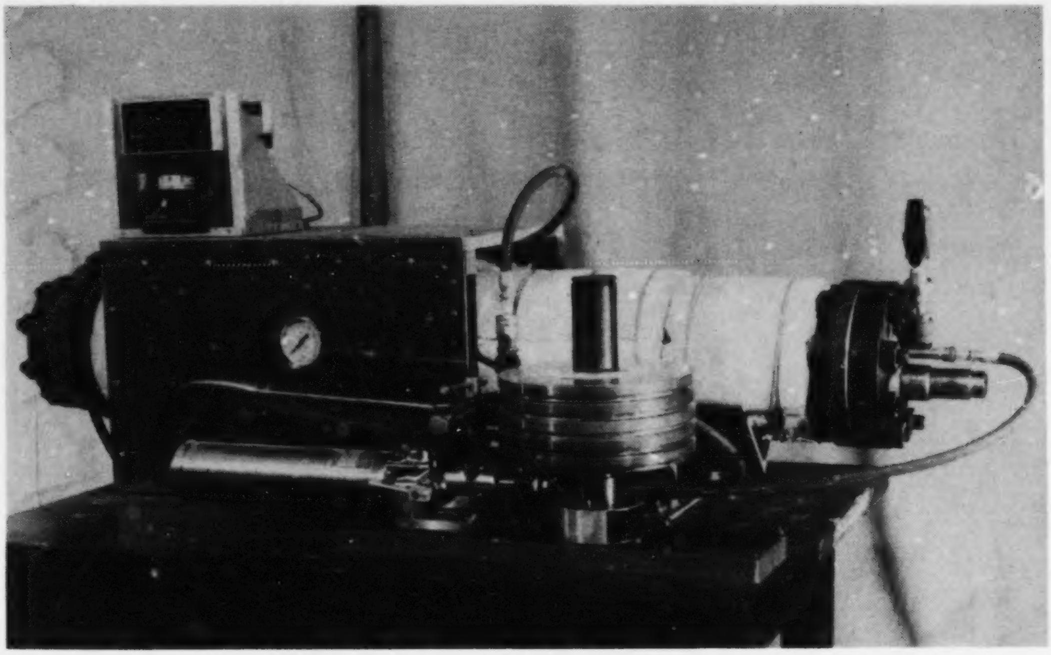

Figure 6. Calibrator assembly for pressure and temperature calibration of the DRI probe

Figure 7. Erection of riser pipe (6 in. diameter) to hold the probe and attached sinker bars before insertion down the well. This well is no. 8-1 of the East Mesa geothermal field

for the downhole test. Figure 8 shows a closer view of the wellhead at well 8-1, illustrating the mounting of the sheave pulley that directs the cable from ground level to the top of the riser pipe.

The cable enters the riser pipe over an upper sheave pulley and through a "lubricator" as shown in Fig. 9. The splashing that is visible in Fig. 9 is necessary until the probe and cable are sufficiently submerged to provide a significant weight downward into the well, after which the rubber collar of the lubricator is tightened around the cable, and splashing ceases. The clamping force of the rubber collar is adjustable, and it is sufficient to lift the entire riser assembly (three 8½-foot pipe sections, plus lubricator) from the wellhead.

V. Downhole Measurement Tools of the Future

a) Downhole sensors

Sensors for use at geothermal temperatures and pressures are probably adequate for the immediate needs of the geothermal industry. Temperature measurement, in particular, is not limited by the severity of geothermal conditions. Pressure sensors are probably adequate up to 500°F, when selected among the alternatives presented by DRI, Sperry-Sun, and present-day strain gauge technology. Above 500°F, however, the limitations imposed by insulating materials are critical, and improvement must come from the employment of inorganic materials .

b) Downhole electronic assemblies

The development of simple amplification circuitry by use of diodes and triodes fabricated from metal-ceramic configurations seems certain to extend the capabilities of downhole measurement, in the near future. However,

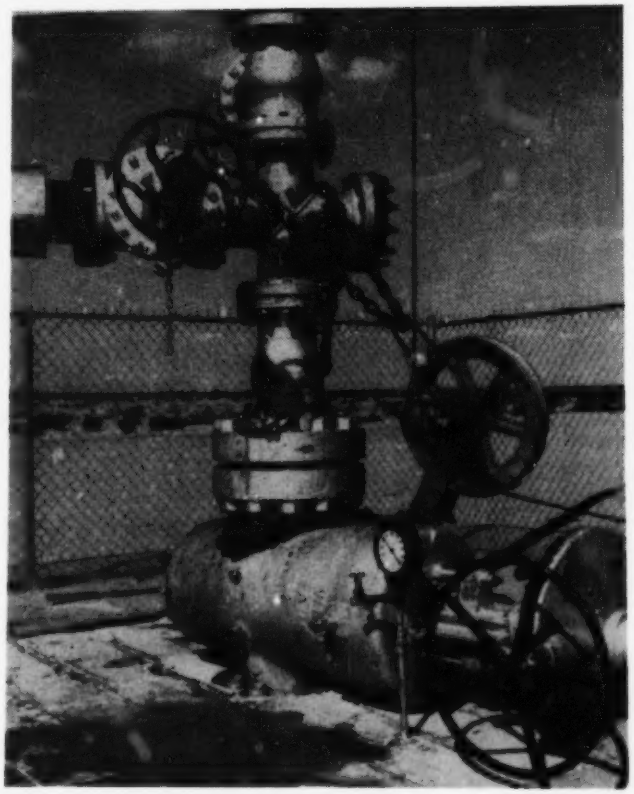

Figure 8. Close-up view of well no. 8-1, showing method of attaching lower sheave pulley for the 7-conductor cable.

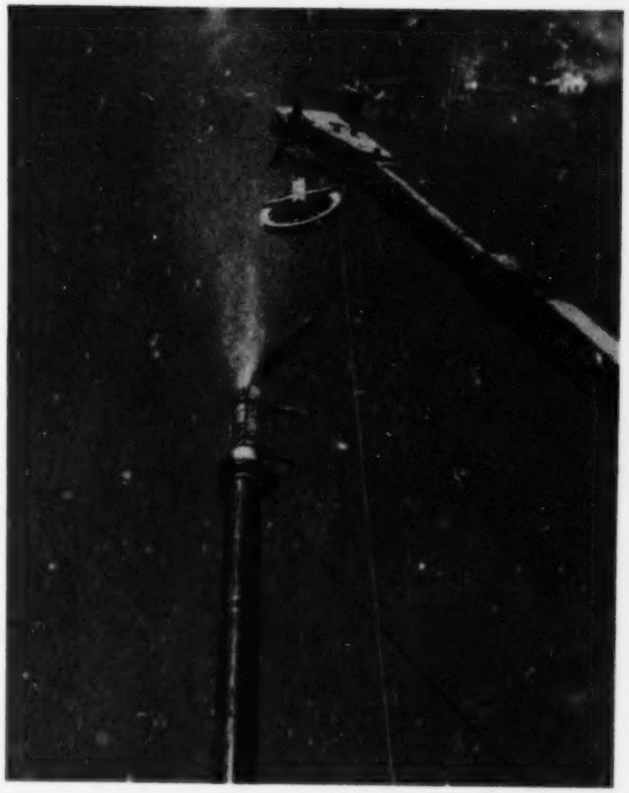

Figure 9. Top of riser pipe, showing cable entering the riser through the lubricator. The blade-shaped device is a cable rest. Splashing occurs when lubricator is not yet clamped tight.

ceramic materials are fundamentally vulnerable to moisture and gas intrusion, and this is a significant development problem in their application as insulators under geothermal conditions.

For the near term, cooling of electronic components by Dewar flasks or other devices offers an ingenious means of obtaining sensitive downhole measurements that are not obtainable by any other means, as demonstrated by the Los Alamos Laboratory.

c) Summary

The present generation of tools for measurement of physical conditions within geothermal wells is subject to an upper temperature limit of about 250°C, mainly due to the limitations imposed by synthetic resin insulating materials. It is reasonable to expect that electronic assemblies with insulation provided by ceramic materials will permit this temperature limitation to be raised. Sampling of fluid within geothermal wells will probably continue to be achieved mainly with mechanical devices, because electrical components such as motors and solenoid valves probably cannot operate at temperatures in excess of 250°C.

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Collection of Chemical, Isotope, and Gas Samples from Geothermal Wells

by

Nancy L. Nehring and Alfred H. Truesdell
U.S. Geological Survey, Menlo Park, Caliornia 94025

ABSTRACT

Reconstruction of the downhole composition in a geothermal well requires field measurements of total fluid enthalpy and separator pressure along with chemical, isotope, and gas analyses of separated water, steam condensate and gas phases. Analyses of each phase for components distributed between phases are necessary because the fluids may not be in equilibrium at the sampling points. Cooling after separation must be sufficient to prevent loss of volatiles and water vapor. The collection and analysis schemes presented are designed to allow complete chemical and gas analyses and isotopic analyses of major carbon, oxygen, hydrogen, and sulfur containing species.

INTRODUCTION

Steam Wells

Steam wells such as those at The Geysers do not present major collection problems in obtaining a representative sample. It is usually sufficient to collect a sample from a bypass on the wellhead, taking precautions to avoid condensation in the bypass. This can be accomplished either by flowing sufficient steam to insure the temperature of the collected steam is the same as that in the well or by insulating a large diameter bypass. A probe inserted to the center of a large diameter flowing steam line has been found to provide representative samples[1/].

Hot Water Wells

Sampling hot water wells is more difficult. Small amounts of fluid must be removed from a rapidly flowing, usually two-phase, fluid in a controlled manner so the samples are representative of the whole fluid. Simply connecting a condenser to a pipe carrying a water-steam mixture does not produce the correct proportion of the two phases. It is possible to collect good samples of the water and steam phases after separation of the two-phase fluid is completed in a cyclone separator and use enthalpy measurements to calculate the total composition.

SEPARATION OF HOT WATER AND STEAM

Understanding the operation and limitations of separators is necessary before reliable samples can be collected. A centrifugal Webre separator (Fig. 1) is provided on most production wells. It consists of a vertical drum with a tangential inlet at the center, an outlet for water at the bottom, and a central outlet tube open at the top which collects the steam. The two-phase fluid enters tangentially at the center, spins rapidly around the outer wall of the drum with the water collecting on the outside and falling to the bottom and the steam moving to the inside and flowing down the central tube. The steam-water level is set by adjustment of a valve in the water flow line. Since water in the steam line to the turbines would be highly undesirable, it is usual to stabilize the water level by allowing a small flow of steam into the water line. If sampling is then done from the water line, apparent nonequilibrium fractionation of gases between steam and water will be observed. Allowing some steam in the water line also would produce slightly lower apparent enthalpy but this can be avoided by careful adjustment of separator water level during enthalpy measurements. Water samples should be taken, if possible, from a separate tap below the water outlet of the separator where the water is less likely to be contaminated with steam (Fig. 1).

If a large separator is not available, the sample can be taken with a mini cyclone separator (Figs. 2 and 3). With this separator the water and steam flows are adjusted to allow some water to issue from the steam outlet while collecting from the water outlet and vice versa. The separator and the tube from the bypass must be well insulated and the flow limited to maintain the pressure in the separator during sampling nearly equal to the pressure in the well. These measures are necessary to insure that condensation does not occur before or in the separator and that the water and steam collected from the separator have the same compositions as the phases in the well.

Enthalpy Measurements

Enthalpy measurements are routinely made on production wells by measuring the flows of steam and water from the large separator. The measurement of total enthalpy without a large separator is difficult and approximate but may be done by critical lip pressure measurements or by measuring the steam/gas ratio at two different pressures[2]. If it is known that boiling in the formation does not occur, the bottom hole flowing temperature can be used to obtain a value for the enthalpy.

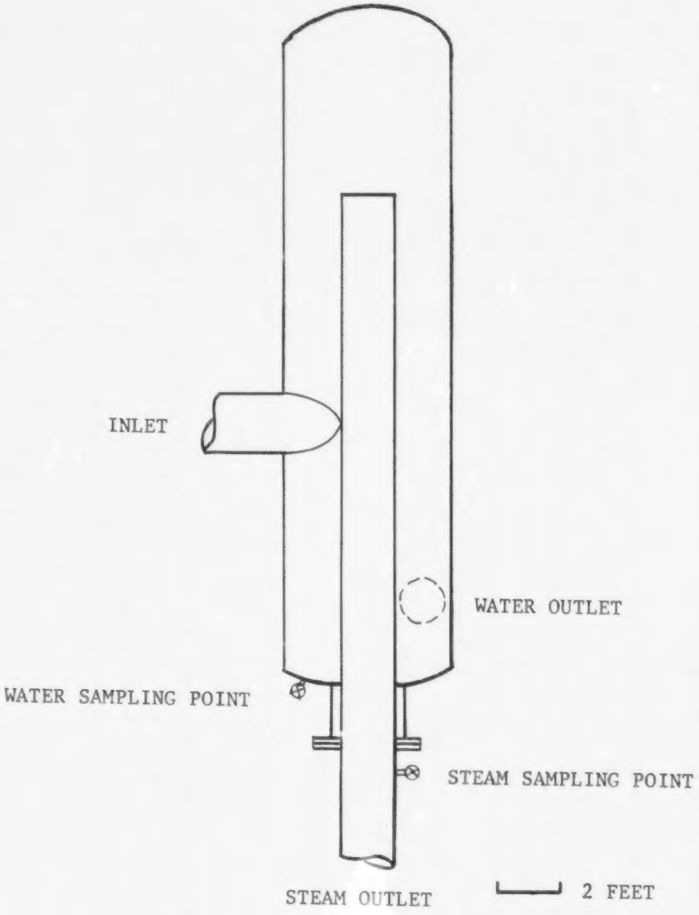
INLET
WATER OUTLET
WATER SAMPLING POINT
STEAM SAMPLING POINT
STEAM OUTLET
2 FEET

Figure 1. Cross Section of Webre Separator showing best sampling points

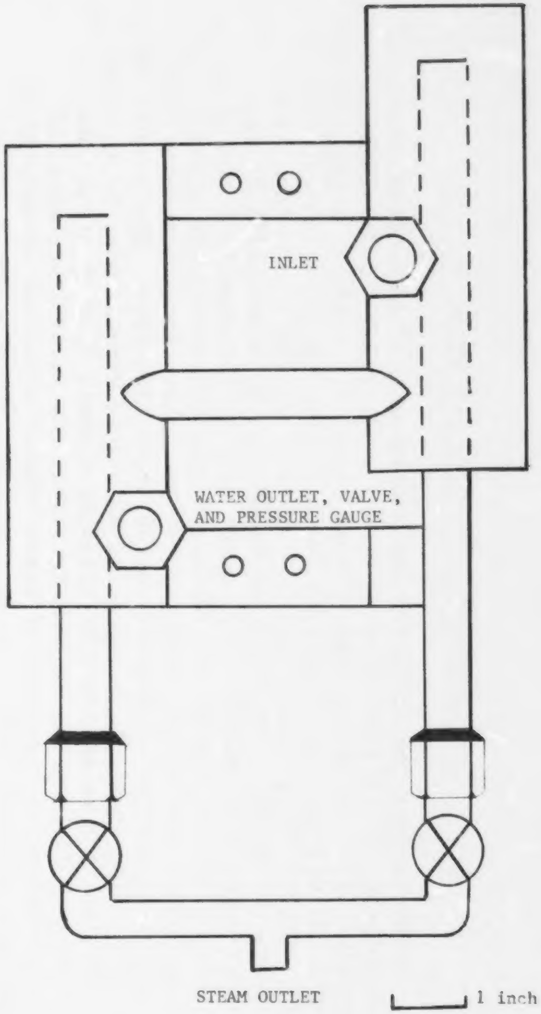
INLET
WATER OUTLET, VALVE,
AND PRESSURE GAUGE
STEAM OUTLET
1 inch

Figure 2. Mini Cyclone Separator of New Zealand design

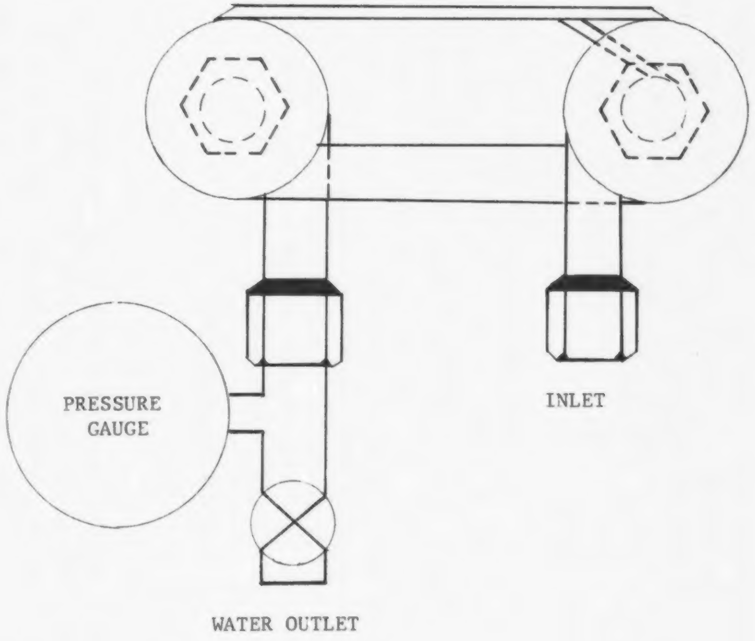
PRESSURE GAUGE
INLET
WATER OUTLET

Figure 3. Top view of Mini Cyclone Separator with pressure gauge attached

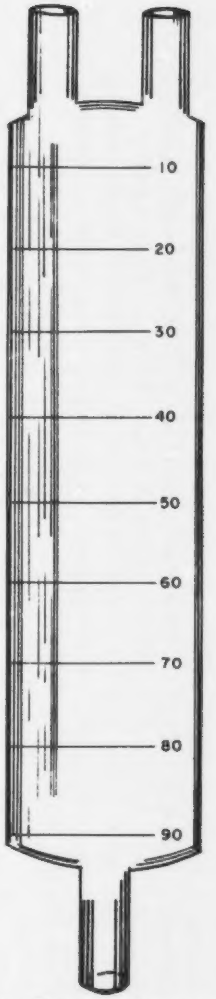
10
20
30
40
50
60
70
80
90

Figure 4. Steam-gas Separator modified from a 100 ml graduated cylinder

CONDENSATION AND COOLING

Steam and water exit from the separator at temperatures considerably above surface boiling and must be cooled for safe handling and to avoid the loss of volatile substances. This is most easily accomplished with a double coil condenser of ¼" stainless steel tubing connected to the separator (or bypass) by a regulating valve. Larger diameter tubing may allow inconveniently large slugs of gas and condensate to form. The first coil is immersed in water which is allowed to boil, effectively reducing the temperature of the fluid sample to 100°C or less. The second coil is held in an ice or water bath or in the air according to the desired temperature of collection. The water and steam phases can be cooled by serial passage through the same condenser but are treated differently when they emerge.

SEPARATION OF STEAM CONDENSATE AND GAS

Collection of steam condensate and gas from a steam well is the same as from a water-steam separator but the methods used may vary because of different steam/gas ratios and because it may be necessary to check for incomplete steam separation in the separator. The steam condensate and gas issue from the condenser in discontinuous slugs. The use of ¼" tubing produces relatively small, uniform slugs and the average composition of issuing fluid is uniform over the period of collection of any single sample.

A sample of gas without the steam condensate is best for gas analyses and for the study of isotopes of carbon, sulfur, and hydrogen in gas components. A steam condensate-gas separator (Fig. 4) was constructed from a graduated cylinder by attaching two tubulations at the top and one at the bottom. The flow from the condenser enters at the top (vinyl tubing is used for all connections) and the flow of condensate from the bottom is restricted with a clamp so that gas alone issues from the remaining top tubulation. The tubing on the bottom is inserted in a large bottle of steam condensate to prevent back flow of air into the separator during gas collection.

FIELD MEASUREMENTS

Steam/Gas Ratios

The steam/gas ratio may be measured by timing the alternate displacement of gas by condensate and vice versa in a bottle with one tube at each end (the least accurate method because during the condensate collection part of the volume is occupied by rising gas bubbles), by measuring the flow of water with a graduated cylinder and the flow of gas with a soap film flow-meter from the gas-water separator (more accurate but requiring exact balancing of flows), or by allowing gas to displace condensate in a tube or separator of known volume and measuring the quantity of condensate displaced (the most accurate field method). None of these field methods measure the quantity of gas dissolved in the condensate which may be a large part of the total when the steam/gas ratio is high. More accurate steam/gas ratios may be obtained from laboratory analyses of steam condensate and gas collected in a single bottle (see below).

pH Measurements

During separation and cooling the pressure of CO_2 is above or near one atmosphere and CO_2-supercharged water or steam condensate issues from the condenser. Part of the CO_2 is rapidly lost and the pH and H_2CO_3, HCO_3 and CO_3 concentrations change until equilibrium with atmospheric CO_2 is established. For this reason pH measurements and field alkalinity titrations are not very useful. It is more useful to collect all the CO_2 by $SrCO_3$ precipitation (described later) and to measure the pH and alkalinity on air-equilibrated samples in the laboratory. This pH measurement can be related to the state of ionization of all weak acids and bases.

Pressure and Temperature Measurements

Separator pressure is needed to calculate the water/steam ratio. Temperature measurements of the water and steam condensate issuing from the condenser are needed to calculate the distribution of gases between phases and are desirable to determine if isotopic fractionation of D or ^{18}O occurred.

COLLECTION OF WATER

Figure 5 is a schematic diagram of the collection procedure discussed in the paper.

Dissolved Salts

Water samples for dissolved salts are filtered through a 0.45 μ pore membrane filter (or if suspended clay is suspected, through a 0.1 μ pore membrane) and part is acidified to pH 2 with HCl to prevent precipitation of Ca or Mg carbonates or adsorption of cations on the walls of the bottle. The dissolved salts are analysed by conventional water chemistry methods. Silica is usually present in amounts exceeding saturation with amorphous silica at room temperature so a separate sample is diluted 1:10 (or 1:20 for fluids originally over 300°C) with silica-free water to prevent precipitation and preserve monomeric silica necessary for the molybdate method. Other preservation methods are required for trace elemental analysis.

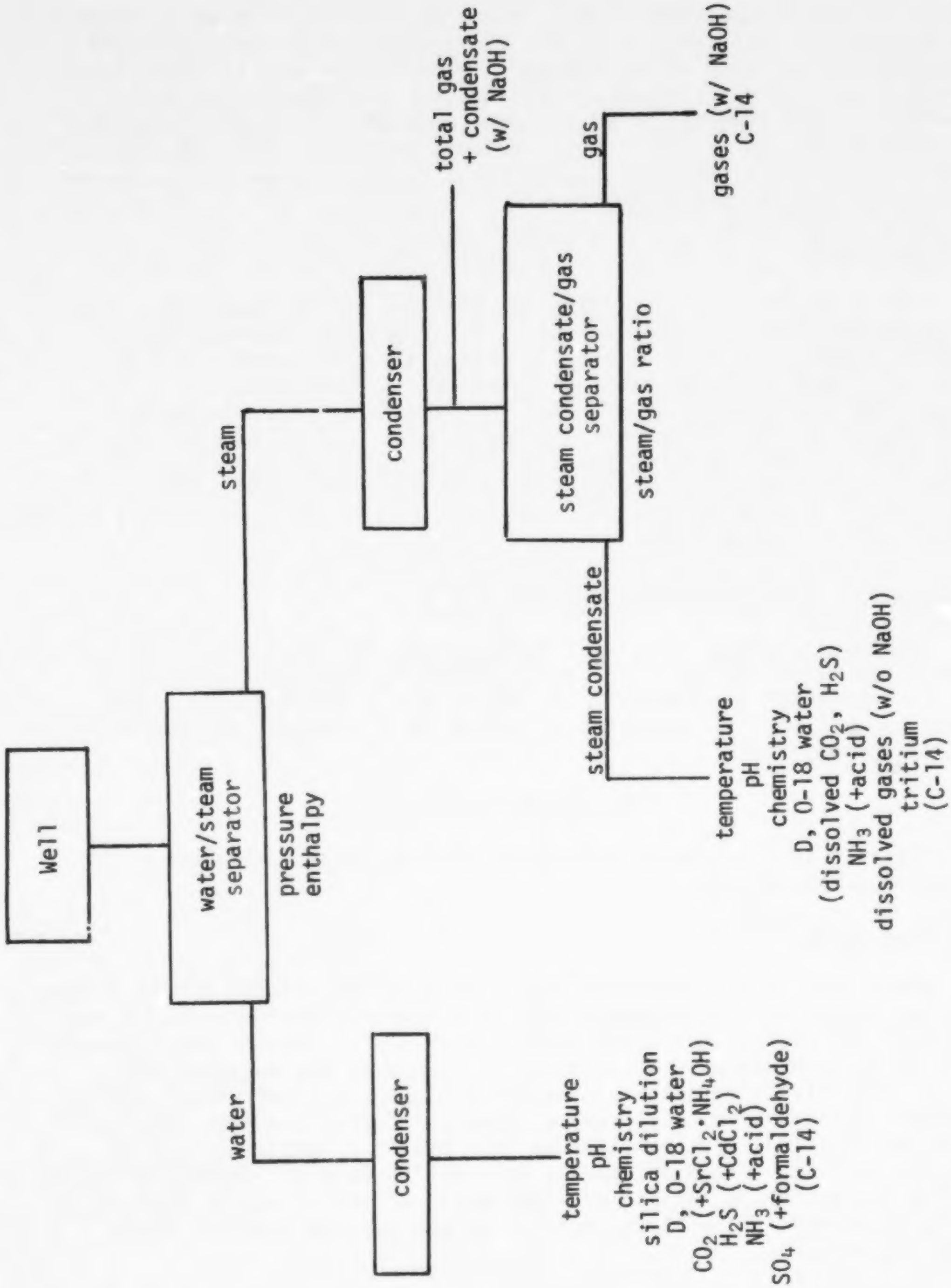
Well
water/steam separator
pressure
enthalpy
water
condenser
temperature
pH
chemistry
silica dilution
D, O-18 water
CO_2 (+$SrCl_2 \cdot NH_4OH$)
H_2S (+$CdCl_2$)
NH_3 (+acid)
SO_4 (+formaldehyde)
(C-14)
steam
condenser
total gas
+ condensate
(w/ NaOH)
steam condensate/gas separator
steam/gas ratio
gas
gases (w/ NaOH)
C-14
steam condensate
temperature
pH
chemistry
D, O-18 water
(dissolved CO_2, H_2S)
NH_3 (+acid)
dissolved gases (w/o NaOH)
tritium
(C-14)

Figure 5. Schematic diagram of sampling procedure

Isotopes

Water samples for isotopic analysis (^{18}O and D) are collected in glass bottles with polyseal caps without filtration (which might allow evaporation). A sample for isotopes in dissolved sulfate (^{18}O and ^{34}S) is collected in one or two liter bottles according to concentration (at least 20-30 mg SO_4 is needed for analysis) and preserved with 4 ml/ℓ of formalin solution to prevent bacterial oxidation of H_2S to SO_4. Collection of dissolved CO_2 for ^{13}C and H_2S for ^{34}S will be discussed under dissolved gases.

Dissolved Gases

Although most gas partitions into the steam phase, enough remains in the water to make analysis of dissolved gases important. The most effective way of preserving CO_2 dissolved in water (not only CO_2 but all carbonate species) is to precipitate $SrCO_3$ in a glass bottle by adding concentrated NH_4OH saturated with $SrCl_2$. The ammonia buffers the solution so that all forms of CO_2 are converted to CO_3 and precipitated. Precipitation must be done immediately because CO_2 is rapidly lost to the atmosphere. Later in the laboratory the sample is filtered, weighed, and saved for isotopic analysis.

Hydrogen sulfide is similarly precipitated as CdS with $CdCl_2$ solution. The addition of buffer is unnecessary because the natural bicarbonate - carbon dioxide buffer maintains the solution at a high enough pH (>3) to prevent loss of H_2S with an excess of Cd present.

Ammonia should be preserved in a sealed bottle, acidified if the discharge is alkaline and analysed as soon as possible. Other dissolved gases may be collected by allowing the water to almost fill a weighed, evacuated gas bottle (Fig. 6) through a vinyl tubing attachment to the condenser. The head space of this bottle is analysed for gases in equilibrium with the water.

COLLECTION OF STEAM CONDENSATE AND GAS

Dissolved Salts

Sampling of condensate may be done directly from the condenser or through the bottom tubulation of the steam condensate-gas separator and preserved as for water samples. Chemical analysis may be limited to boron, ammonia, bicarbonate and other substances that have volatile forms that may be carried in steam. On samples from a separator it is necessary to determine the completeness of the separation by analysis of the condensate for Cl, Na, or another nonvolatile substance.

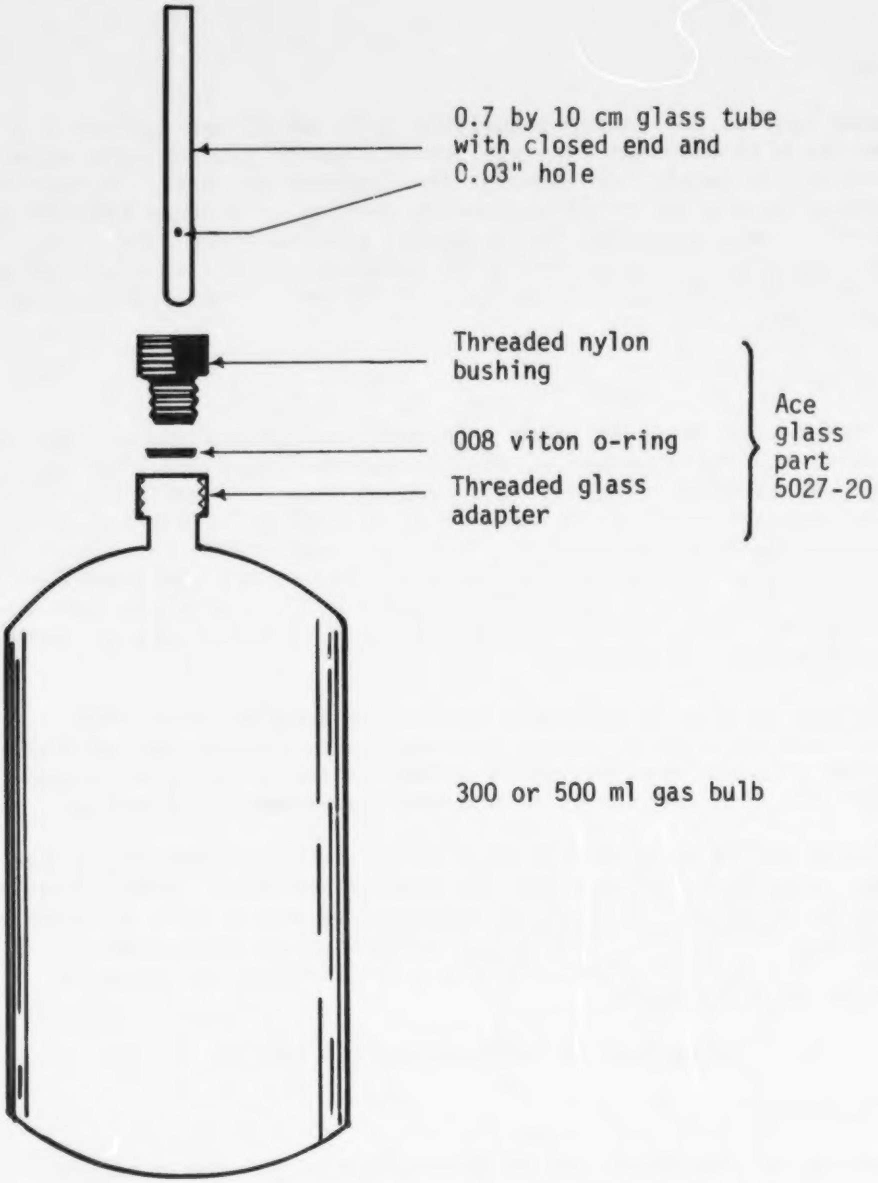
0.7 by 10 cm glass tube with closed end and 0.03" hole
Threaded nylon bushing
008 viton o-ring
Threaded glass adapter
Ace glass part 5027-20
300 or 500 ml gas bulb

Figure 6. Exploded view of gas sample bottle. The bottle is opened by sliding the hole inside the o-ring. The tube may be evacuated with the bottle closed by clamping a second o-ring and washer to the top of the adapter. Gas bottles with NaOH solution are evacuated by a water aspirator with gentle boiling of the solution.

Isotopes

Condensate samples for ^{18}O and D are collected as described above. Sulfate is only contained in steam condensate if produced by the oxidation of H_2S and is not collected for isotopic analysis. CO_2 and H_2S may be precipitated as described above from the condensate or separated from the caustic in the gas bottle (described later). Fractionations resulting from solution of gases in water are small and either of these separates may be analysed depending on which contains the major amount of the gas.

Tritium and carbon-14 may allow limits to be placed on the age of geothermal fluids or on the amount of dilution by near surface water. The analyses are difficult and costly and geothermal fluids contain very little of these isotopes so the collection should be carefully made to avoid contamination. A steam condensate sample should be collected for tritium, as a brine sample requires distillation to remove the salts. Dry, clean bottles should be well flushed by flowing the sample through vinyl tubing to the bottom of the bottle and allowing the bottle to overflow for some time. The bottle should then be sealed with a polyseal cap and taped with vinyl electrical tape applied in the clockwise direction.

Carbon-14 can be collected from steam condensate by precipitation of $SrCO_3$, but the amount of sample (>3 gms of carbon usually needed for analysis) requires long settling times. The collection of steam phase CO_2 from the gas-water separator into gas bubblers containing CO_2-free ammonia may be quicker and is less prone to contamination. If the steam/gas ratio is very high this method may require inconveniently long collection times, and $SrCO_3$ precipitation from steam condensate may be preferred.

Gases

The total cooled steam sample (gas and condensate) is collected into an evacuated 300 or 500 ml gas bottle (Fig. 6) containing 50 to 100 ml of 4N NaOH (prepared as carbonate-free as possible). The flow from the condenser should be reduced by regulating the valve on the separator or steam bypass. A pressure-relief valve may be used to prevent over-pressuring the gas bottle. This sample allows the most accurate measurement of steam, CO_2 and H_2S but the quantity of residual gases may be too small for some determinations. In this case a gas-only sample (without condensate) may be collected from the top of the gas-water separator. A larger quantity of caustic (100 to 150 ml) may be required because a larger quantity of CO_2 and H_2S will be collected.

The flow of gas into the bottle may at first exceed the flow into the gas-water separator and the gas flow into the bottle should be restricted by pinching the vinyl tubing until a balance is achieved. Shaking the gas bottle increases the rate of CO_2 and H_2S absorption and may be necessary at the end, although allowing the gas to bubble through the caustic produces adequate absorption during most of the collection. The CO_2 and H_2S analyses are obtained by wet chemical analysis of NaOH solution. The other gases are analysed by gas chromatography. Dissolved NH_3, CO_2, and H_2S in the steam condensate may be collected and analysed by the same methods described above for water.

[1] J. Farison, Oral commun., 1977.

[2] James, Russel, 1964, Alternate methods of determining enthalpy and mass flow: Proc. U.N. Conf. on New Sources of Energy, Rome, 1961, v. 2, p. 265-267.

GEOTHERMAL DOWNHOLE SAMPLING INSTRUMENTATION

R. Fournier and J. M. Thompson
U. S. Geological Survey, Menlo Park, California

A sampling device 5 cm in outside diameter, with an internal volume of about 500 ml has been designed to collect liquid and gas samples in wells where both steam and water are present at temperatures up to about 280°C. Detailed plans for construction of the sampler have been published by Fournier and Morganstern (1971). A long flexible stainless steel tube serves as the support cable. The sample device is lowered in the open position and fluid flows through it during its descent. This procedure circumvents the flashing of water to steam and preferential partitioning of volatiles into the sampler that may occur when an evacuated chamber is opened at the point of collection. Closure is accomplished by gas pressure applied from the surface through the flexible tube to a piston and plunger within the sample chamber. Any nonreactive gas is a suitable pressure medium. Continued application of gas pressure during withdrawal of the device prevents leakage, either into or out of the sample chamber that otherwise may be caused by changing conditions of temperature and pressure. The sampling device has been used successfully to collect water and gas samples from research holes drilled in hot-springs areas of Yellowstone National

Park, Wyoming. The main limitation to the use of the device is the need for using a flexible stainless steel tube as long as the well is deep. At least one commercially available down-hole pressure measuring instrument uses a long, flexible stainless steel tube for its operation, and it may be possible to use the same tube in combination with the sampler described here to collect down-hole water and gas samples.

A second down-hole sampler is now being tested that is similar in basic design to the first sampler, but is suspended on a wireline and is closed by a spring-loaded mechanism triggered by an inertial mass. The mass operates in a similar manner to the one described by Klyen (1973): at the depth where a water and gas sample is to be collected the sampler is allowed to drop as quickly as possible for about 3 to 5 meters and then is brought to a sudden stop. An inertial mass, suspended on a string, continues its downward movement and triggers the closure mechanism.

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ABSTRACT

CASE HISTORY OF GEOTHERMAL EFFLUENTS SAMPLING FOR FOUR GEOTHERMAL WELLS

G. R. Conner and P. B. Needham, Jr.
College Park Metallurgy Research Center
Bureau of Mines, U. S. Department of the Interior
College Park, Maryland

Detailed studies of the chemical nature of flowing geothermal brines have been conducted for the past 2 years at geothermal wells located in the Imperial Valley of California. These continous onsite brine analyses are being carried out in support of a Bureau of Mines' geothermal test facility designed to study the serious corrosion and scaling processes associated with resource recovery from these brines.

Corrosion studies have been conducted on two geothermal reservoirs of the Imperial Valley; (1) the Salton Sea geothermal field (geothermal wells Magmamax #1 and Woolsey #1), with brines ranging from 24 to 32 wt-pct total dissolved solids (TDS), pressures ranging from 250 to 500 psig, and temperatures ranging from 180° to 305° C; and (2) the East Mesa geothermal field (geothermal wells Mesa 6-1 and Mesa 6-2), with brines ranging from 1 to 7 wt-pct TDS, pressures ranging from 100 to 200 psig, and temperatures ranging from 100° to 200° C. An important step to understanding the observed corrosion and scaling phenomena is the development of the proper model of the chemical environment for a flowing geothermal brine. To develop such a model, accurate elemental determinations, a determination of the major chemical ions, pH determinations, and accurate gas component determinations must be obtained.

Analytical procedures have been developed to determine the major anions in solution (chloride and carbonate species) by titration techniques. Determinations of pH have been made by usual methods. Analytical procedures are described for the determination of 10 major brine constituents (Na, Ca, K, Li, Sr, Mn, Fe, Pb, Cu, and Ag) by atomic absorption spectroscopy (AAS) and for the determination of gaseous components in the brine (O_2, N_2, H_2, CH_4, and H_2S) by gas chromatography (GC).

Procedures for extracting the brine samples from operating geothermal systems were developed for the wet chemical, AAS, and GC analysis. Studies were made of various types of sample-condensing coils, the location of sampling ports with respect to flow, various brine-flow patterns, and the effect on the chemical analyses of pipe, valves, and elbow geometries. The use of chemical additives to the brine samples in order to preserve species in solution for AAS and carbonate analysis is also described.

Results will be discussed for tests on the East Mesa geothermal field during 1975 and on the Salton Sea geothermal field in 1976. These results have shown that the dynamic nature of the chemistry of brines flowing from geothermal wells requires constant onsite monitoring of the major brine constituents. In particular, the onsite chemical studies have clearly shown the dependence of the observed brine chemistry on (1) the brine flowrate from the well, (2) reservoir and/or well design engineering changes, and (3) the total operating time of the geothermal well. In addition substantial differences were also noted in the chemical makeup of individual geothermal wells located on the same geothermal field. These results, therefore, show that each of these conditions is an important parameter that must be reported with any reliable brine chemical analysis.

ABSTRACT

ESTIMATION OF POLLUTANT CHARACTERISTICS FROM GEOCHEMICAL SURFACE INVESTIGATIONS

F. B. Tonani, Geochemex, and
H. T. Meidav, Geonomics, Inc., Berkeley, Calif.

Estimation of reservoir chemistry is ipso facto an estimation of pollution potential due to leakage of effluents during exploration or production from that reservoir. The estimation of reservoir chemistry is one of the important goals of field chemistry.

Reservoir chemistry may be estimated under a variety of conditions and in many different ways:

1. When the water issuing in a hot spring is proven to be a direct leakage of reservoir water (and hence chemical thermometry may be applied in its simplest form).

2. When the spring or well water is a mixture of reservoir water and, for example, shallow groundwater, mixing models are utilized to determine geochemical temperatures, and concurrently resulting in estimation of true reservoir chemistry.

3. When a mixing model cannot be determined, based upon the chemical analysis itself, external constraints can be used to determine the mixing models. Such constraints may be other types of data, such as electrical resistivity. When a reasonable estimate of reservoir temperature may be made, a correlation of temperature vs. salinity may result in a similar constraint.

4. In absence of specific information about the reservoir water, statistics of chemical composition of underground or surface water in the same general area usually provides a reasonable prediction of reservoir chemistry.

5. When a fumarole occurs in the area, the gas chemistry can be employed to infer the composition of the liquid phase, through the computation of chemical equilibrium. This applies strictly to volatile substances, but previous knowledge of correlation between the volatile substances and other dissolved constituents may result in estimates of the composition of reservoir water.

ESTIMATION OF POLLUTANT CHARACTERISTICS FROM GEOCHEMICAL SURFACE INVESTIGATIONS

F. Tonani and H. T. Meidav

Knowledge of the chemical composition of the water and gas phases in fluids produced from a geothermal reservoir is part of a series of iterations whereby an increasing refinement of the information is possible with increasing details of exploration. In the initial phase of exploration, only broad knowledge of the geothermal system can be expected from surface reconnaissance. As the knowledge of the reservoir improves because of increased exploration activity, the drilling of some exploration holes, and the production of those holes, a finer and finer understanding and knowledge of reservoir chemistry becomes possible.

Geochemical exploration, like all other surface-types of exploration, is a process of establishing a geological-chemical model of the system. If that model turns out to be promising from a geothermal exploration point of view (especially when the chemical data are supported by other types of data, such as geophysical data), drilling activity will probably follow, to test the viability of assumptions regarding the reservoir. However, a great deal may be said about the geochemical nature of reservoir fluids from surface investigations. For the future developer of the geothermal reservoir, it is important to know whether considerable problems due to unique chemistry or unique pollution or corrosion problems are likely to occur, because such potential problems may affect the economics of the entire operation. In our discussion, we wish to provide some insights on how, in general, we can assess the gross chemical characteristics of a reservoir from the data of water and gas analyses that are obtainable on the surface.

It is important to keep in mind that in many classical geothermal areas, a considerable natural flow of water and gases has been going on over extended periods of time. Under such circumstances, by studying the chemical composition of the fluids coming to the surface of the earth and discharging to the atmosphere, it might be possible to estimate the change that occurs in natural emission as the result of intensive production from the reservoir. Under very large scale production conditions, it is permissible to think about environmental improvement which might result from a controlled geothermal production. For example, the amount of energy that is continuously being released by a large power plant, such as The Geysers geothermal field power plant complex, is equivalent, over a period of several years of production, to the total amount of energy released by a large volcanic eruption. Hence, it is conceivable that under the geological conditions in some geothermal areas, besides the reduction of efflux to the environment through hot springs and fumaroles in the area, the extraction of energy may result in a measure of control over potential volcanic eruptions which would have brought to the surface a large amount of solid, liquid, and gaseous materials. This is especially true when the volcanic activity may be shown to be related to hydrothermal activity within the upper part of the crust such as at Pozzuoli near Naples, Italy. An underlying axiom is that the release of energy is directly related to the release of chemicals to the atmosphere and vice versa. However, the study of the potential change in the environment from the point of view of effluent discharge reduction is not the main thrust of this paper.

There are a number of ways by which the reservoir chemistry may be estimated. A variety of geological and chemical field conditions affect the chemistry of the fluid which issues at the surface, and hence, a number of different approaches must be employed to estimate reservoir chemistry.

Case 1: Direct Sampling of Reservoir Water (Figure 1)

Under the simplest conditions, the water issuing in a hot spring at the surface is an actual sample of direct leakage from the reservoir at depth. In such a case, chemical analysis of surface water would provide an estimate of reservoir chemistry. The assumptions made in assessing reservoir chemistry in this simplest case is that : (1) little or no re-equilibration or change in composition occurs at lower temperatures as the water flows from the reservoir to the surface, and (2) the hot water

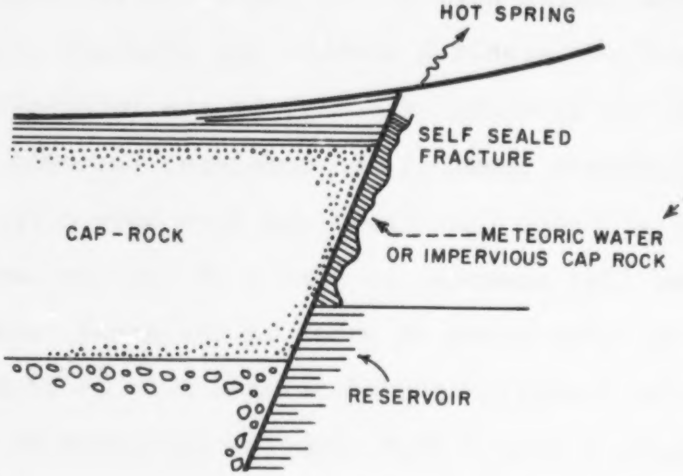
HOT SPRING
SELF SEALED FRACTURE
CAP-ROCK
METEORIC WATER OR IMPERVIOUS CAP ROCK
RESERVOIR

Figure 1. Direct sampling of reservoir water--some hot springs result from uncontaminated reservoir water.

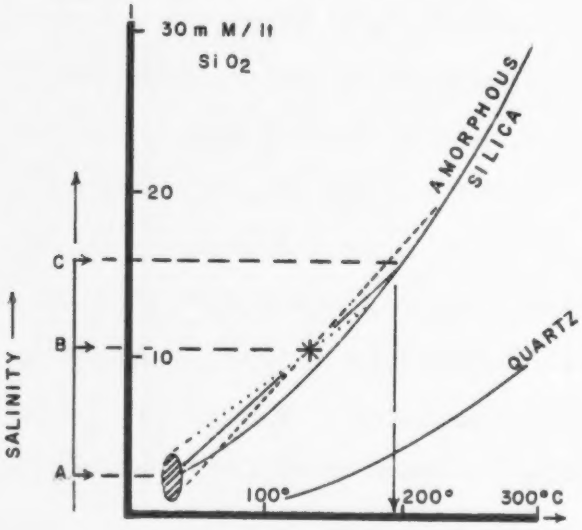

Figure 2. Simple mixing model. The mixing problem is solved by using chemical data and internal data (in this case the solubility of silica).
A: salinity of surface waters in the area
B: salinity of mixed sample of reservoir and surface water
C: salinity of reservoir water.
The mixing model was introduced to calculate reservoir temperature (vertical arrow).

coming from great depth does not mix with cooler, shallow ground water. The test to establish whether the simplest case of direct sampling holds is provided, firstly, by the internal consistency between the different chemical thermometers; secondly, from other lines of evidence that the fluid does indeed represent reservoir water (for example, by virtue of its similarity or difference from other types of water in the area), and thirdly, by evidence from totally independent data such as geophysical data which suggests that a high temperature system does occur in the same area.

Case 2: A Simple Mixing Model (Figures 2 through 4)

Fournier et al. (1974) have suggested a methodology to calculate reservoir temperature by means of measuring the chemistry of both hot and cold springs in the area. By setting up two equations in two unknowns, they have shown that it is possible to estimate the fraction of original reservoir fluid that has risen upward and has mixed with shallower ground water. If the fundamental assumptions made by Fournier et al. hold for a certain set of geological conditions, it is possible to estimate the original chemistry of the reservoir by repeating the same calculations that they have made for the purpose of reconstituting the original reservoir silica content or reservoir temperature.

A large number of chemical constituents or chemical ratios may be employed in order to estimate original reservoir chemistry

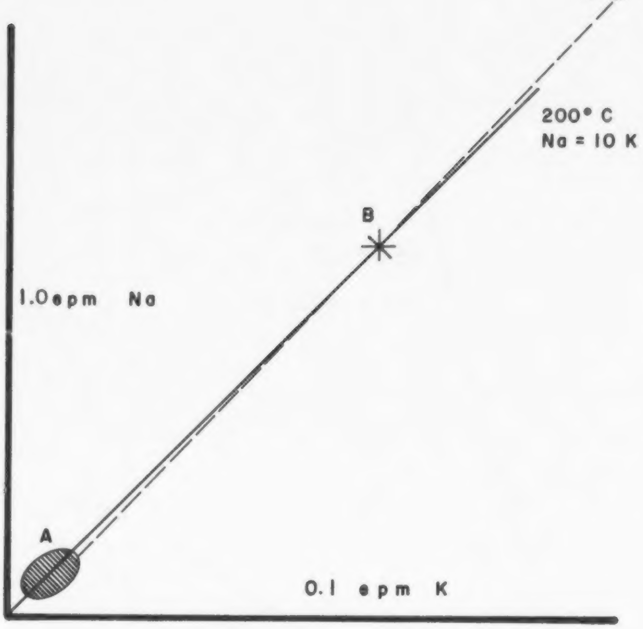
C
200° C
Na = 10 K
B
1.0 epm Na
A
0.1 epm K

Figure 3. Simple mixing model. Sodium to potassium ratio is not affected by dilution by surface waters. The mixed sample of reservoir and surface water does not carry relevant information about reservoir water.

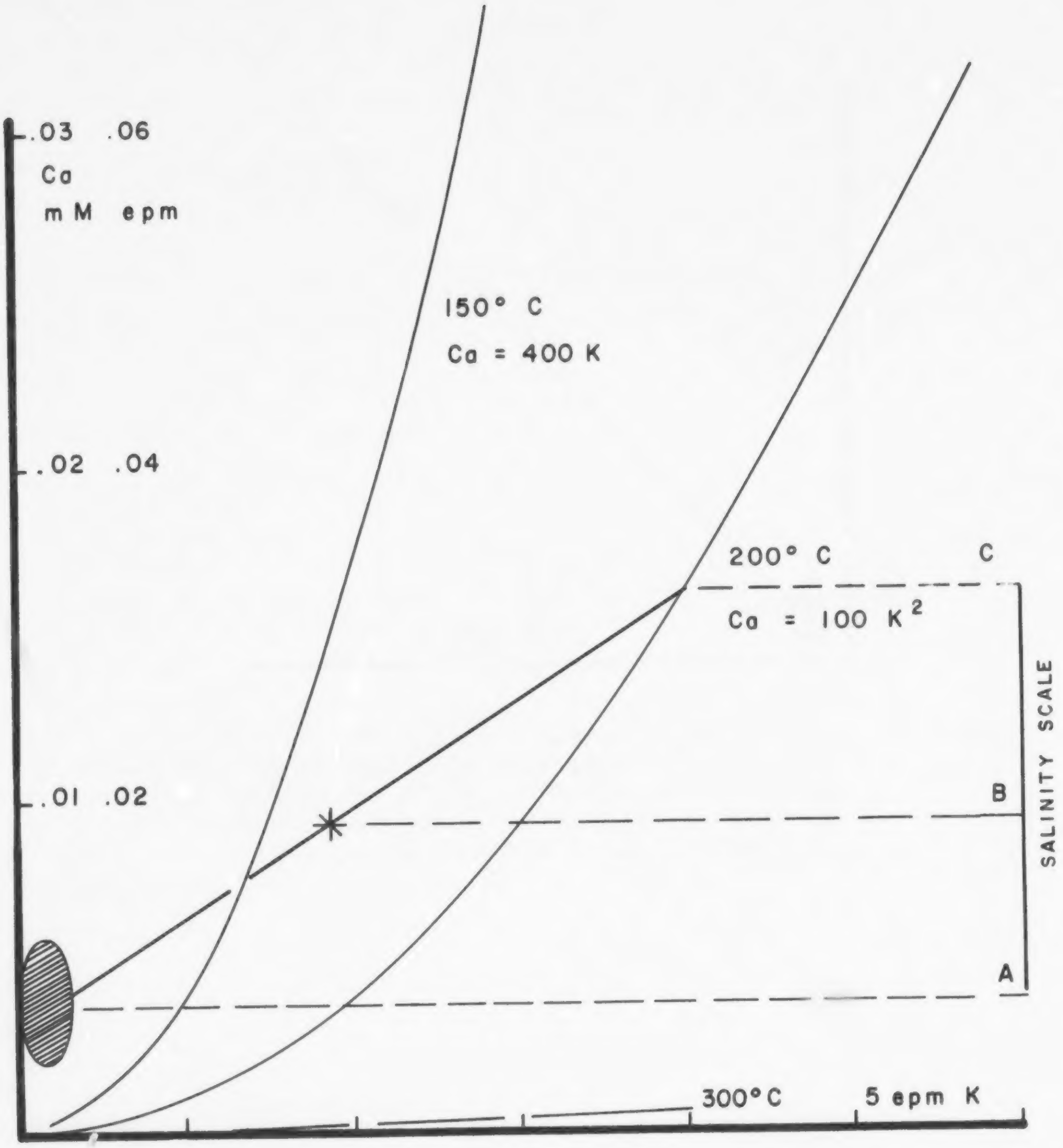

Figure 4. Simple mixing model. One more non-linear relationship of chemical equilibrium.
A: salinity of surface waters in the area
B: salinity of mixed sample of reservoir and surface water
C: salinity of reservoir water.
As opposed to the silica graph, the reservoir temperature is not estimated from this graph.

or the amount of mixing of two different water systems. The sodium-potassium thermometer does not allow the calculation of the amount of dilution by mixing with fresh ground water, because the ratio does not change when dilution with pure or nearly pure water takes place. The silica method does allow the calculation of the amount of dilution, because the solubility curve of silica is non-linear. On the other hand, if we have been successful at estimating the original temperature reservoir and, additionally, we have information about the calcium-potassium ratio, we are in the position of establishing the degree of dilution because the Ca-K ratio is the ratio of the square root of calcium over potassium and as such is affected by dilution or mixing.

Case 3: The Complex Mixing Model (Figures 5 through 7)

In many situations, the conditions which are required by the simple mixing model described above are not fulfilled. In such cases, we have a complex mixing model and external constraints would be necessary to solve the mixing problem. Cases where the simple mixing model may not apply are: (1) when the spread of silica content in surface water is exceedingly large or when the percentage of reservoir water mixing with surface water is very small; (2) a decision cannot be made as to which of the different silica solubility curves applies in the case under consideration; (3) the use of the Ca-K relationship is inapplicable because of precipitation of the calcium as

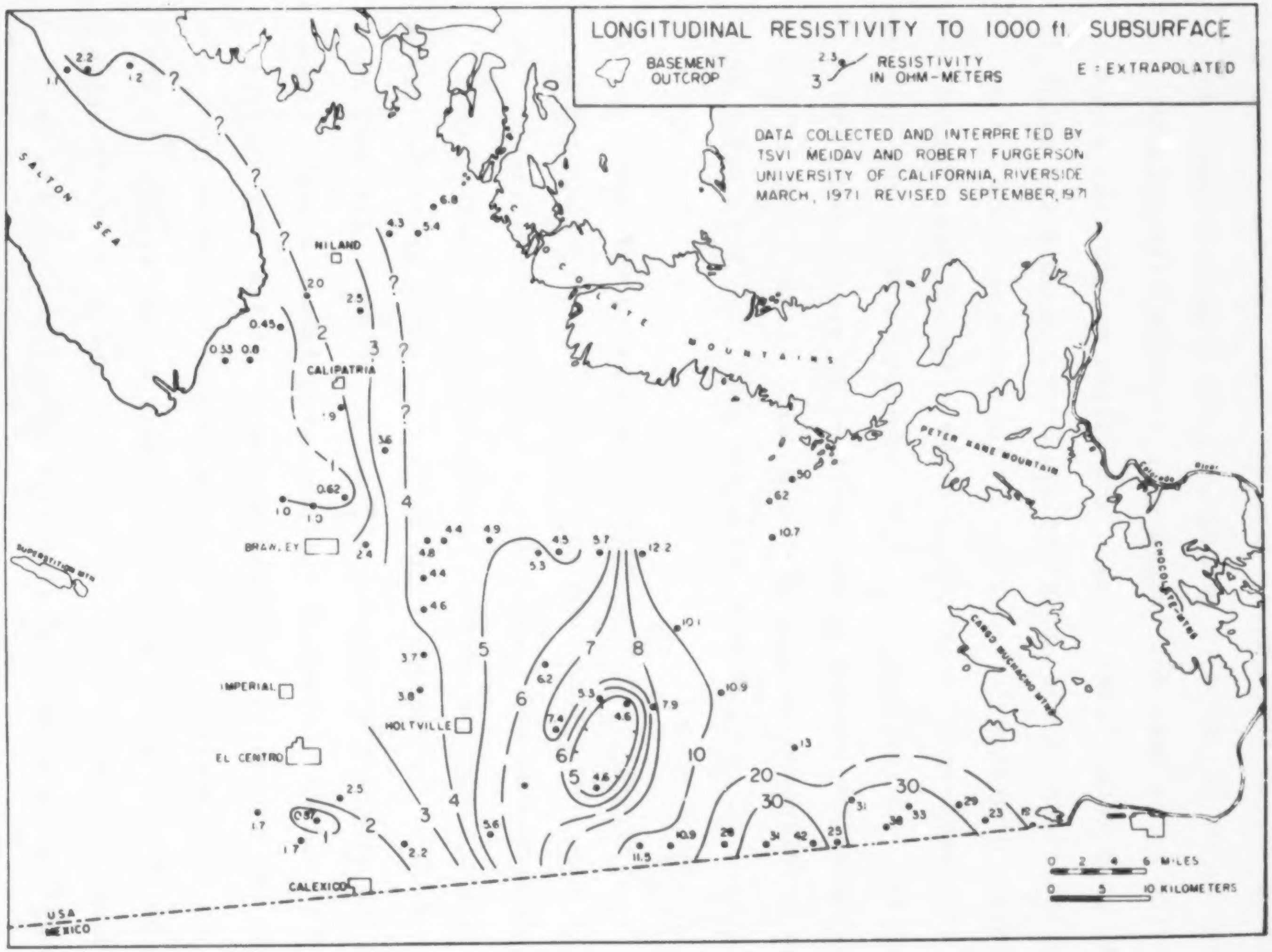
LONGITUDINAL RESISTIVITY TO 1000 ft. SUBSURFACE
BASEMENT OUTCROP
RESISTIVITY IN OHM-METERS
E : EXTRAPOLATED
DATA COLLECTED AND INTERPRETED BY
TSVI MEIDAV AND ROBERT FURGERSON
UNIVERSITY OF CALIFORNIA, RIVERSIDE
MARCH, 1971 REVISED SEPTEMBER, 1971
SALTON SEA
NILAND
CALIPATRIA
BRAWLEY
IMPERIAL
EL CENTRO
HOLTVILLE
CALEXICO
SUPERSTITION MTN
CHOCOLATE MOUNTAINS
PETER KANE MOUNTAIN
CHOCOLATE MTNS
CARGO MUCHACHO MTNS
Colorado River
USA
MEXICO
0 2 4 6 MILES
0 5 10 KILOMETERS

Figure 5.

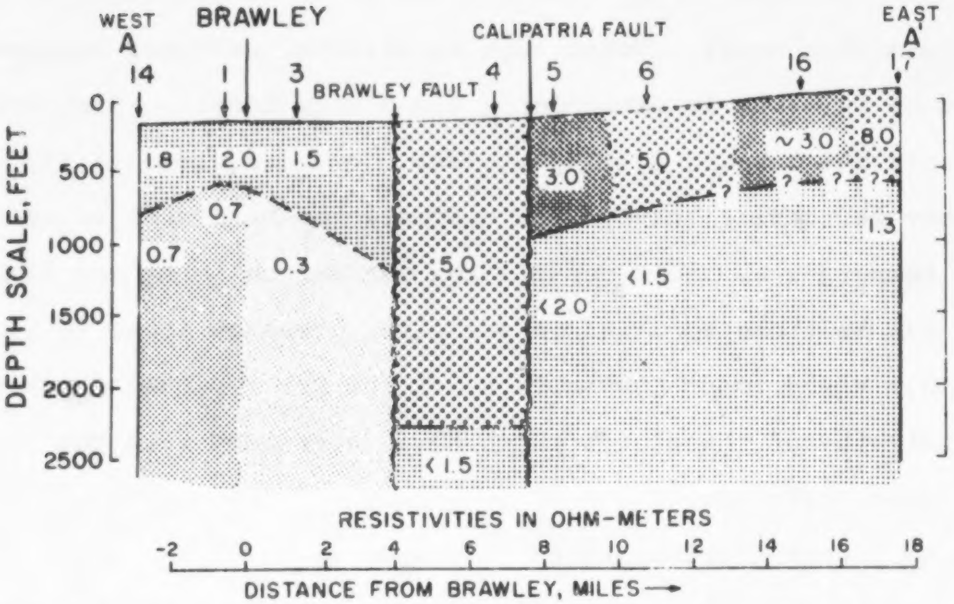
WEST
A
BRAWLEY
CALIPATRIA FAULT
EAST
A'
14
1
3
BRAWLEY FAULT
4
5
6
16
17
0
500
1000
1500
2000
2500
DEPTH SCALE, FEET
1.8
2.0
1.5
0.7
0.7
0.3
5.0
<1.5
3.0
5.0
~3.0
8.0
?
1.3
<1.5
<2.0
RESISTIVITIES IN OHM-METERS
-2
0
2
4
6
8
10
12
14
16
18
DISTANCE FROM BRAWLEY, MILES

Figure 6. Geoelectric cross-section A-A', Brawley Traverse.

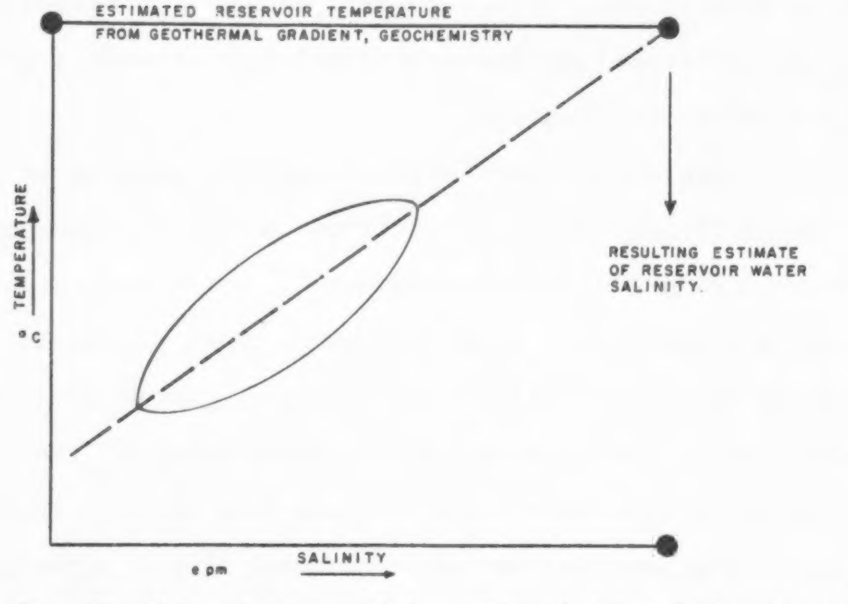

Figure 7. Complex mixing model. Correlation between salinity and temperature due to broad mixing process plus information on reservoir temperature result in a constraint on possible reservoir water salinity.

calcium carbonate, which violates one of the assumptions of the simple mixing model. Under such conditions, external constraints would be valuable in determining the mixing models. Such constraints may come, for example, from electrical resistivity data. In many geothermal surveys, an estimate has been made of reservoir temperature. If a correlation between salinity and temperature can be shown to exist in the given prospect area, it is then possible to estimate the salinity of the reservoir at depth from the salinity of the fluids which have intermixed with the shallower reservoir.

Case 4: Statistical Approach (Figure 8)

In the absence of specific information about the reservoir water, and where either simple mixing models are not considered valid, or complex mixing models do not provide a straightforward solution, a statistical analysis approach may provide a gross estimate of reservoir chemistry.

One objective of any geochemical sampling program is to distinguish the different types of reservoir water that are prevalent within a given area and the boundaries of their distribution. The results and analysis of the different types of water, combined with other types of information such as geophysical data, thermometric data, etc., are aimed at determining which of the different types of water is representative of reservoir water. In the Larderello case, the sampling of water issuing from a formation in the region provides a statistical sampling of the composition of the reservoir water. In

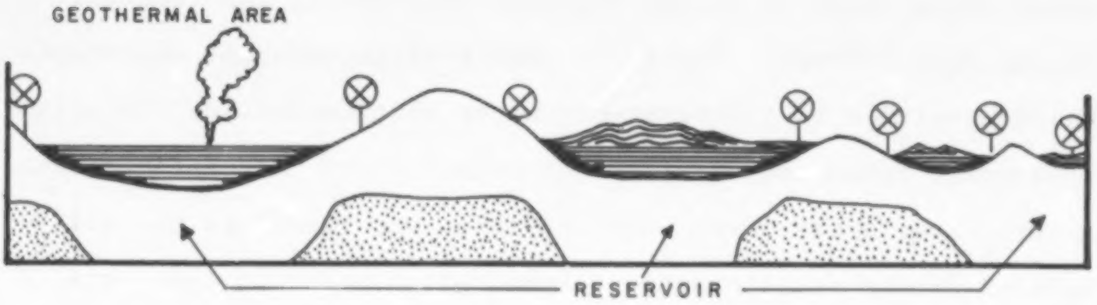

Figure 8. Samples from the same reservoir formation, having essentially the same composition as reservoir water, occur over a vast region wherever the reservoir formation outcrops or comes close to surface. This forms the basis for a statistical approach to estimating reservoir water chemistry.

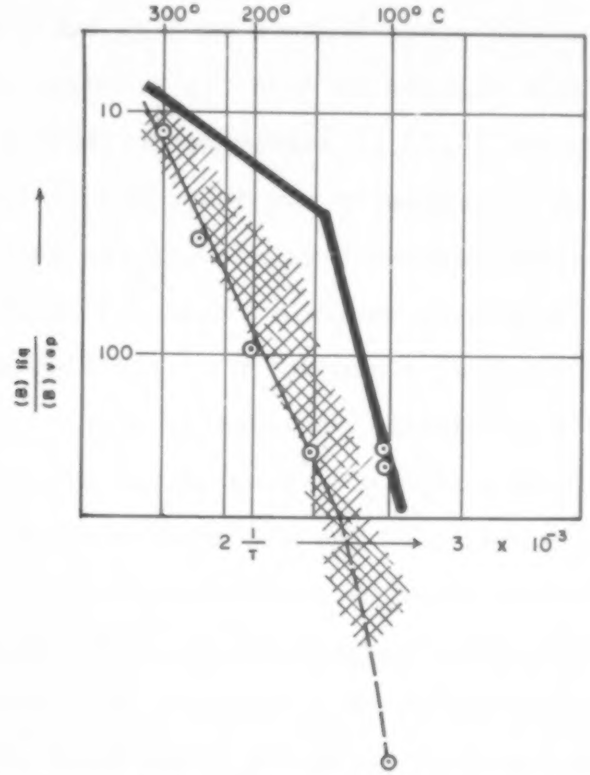

Figure 9. Concentration of boric acid in reservoir water can be estimated from temperature and from concentration in dry steam--graph shows available information to date. Coarsely hatched band may be considered consensus correlation.

other cases, such as in The Geysers, California, the reservoir is not well defined. There, we make inferences about the chemical composition of the reservoir water which underlies the steam reservoir, based upon analyses of both hot and cold springs over a very large area. Even when the reservoir itself is not well-defined from a stratigraphic, lithological point of view, the reservoir may be defined as an aquifer, by virtue of a constant or uniformly varying composition of reservoir water. Systematic sampling of deep ground water over a large area would provide an inference regarding the original composition of the geothermal system before various other factors such as outflow, concentration, and heat have changed it from its original state. For example, The Geysers field is surrounded by sodium-chloride-type water which would give rise to the inference that the deeper water in The Geysers reservoir is also of the NaCl type. In the case of a vapor-dominated system such as The Geysers, uncertainty remains as to the actual composition of the liquid phase of the reservoir because of possible changes in composition that may have taken place as a result of evaporation and heat effects. Some of these uncertainties may be resolved by other methods such as those described below under Case 5.

Case 5: Inferences from Physical-Chemical Relations (Figure 9)

The content of different substances in dry steam depends primarily on the chemical constitution of the reservoir water. We may cite an example of this type: the content of boric acid in the steam is directly proportional to the content of boric acid in the reservoir fluids, where the proportionality constant is dependent upon temperature. By corollary, if we have sufficient statistics of the boron/chloride ratio in the characteristic reservoir water of the particular geothermal system in the area, we can then estimate the chloride content of the geothermal brine, and therefore of the sodium chloride of the brine. The same reasoning may be applied to the relationship between boron and other chemical constitutents. It might be difficult to employ boric acid as an indicator under conditions where condensation of steam may take place before the steam has reached the ground surface. In such a case, other indicators, such as ammonia content, may be valuable for determining reservoir composition, utilizing the same reasoning as above.

In summary, we have attempted to indicate a number of techniques by which the pollutant characteristics of geothermal systems may be estimated from geochemical surface investigations of both liquids and gases. In any of the above cases, the assumptions and calculations that may be made are based upon conceptual models. The veracity of estimates depends to a large extent on the accuracy of any one model. Quite naturally, initial estimates on reservoir composition would improve with the continued exploration in a given area, where more and more representative samples of reservoir fluids would be obtained in the course of increasingly deeper drilling.

ABSTRACT

SAMPLING AND ANALYSIS OF GEOTHERMAL BRINES FROM NILAND FIELD, CALIFORNIA

H. K. Bishop
San Diego Gas & Electric Company, San Diego, California

The Salton Sea Geothermal Field which lies just south of the Salton Sea in the Imperial Valley of Southern California produces a highly saline brine. Development of this resource requires that the properties of the geothermal fluids be fully understood. Currently, San Diego Gas & Electric (SDG&E) in cooperation with the U.S. Energy Research & Development Administration has constructed and is operating a 10-MW Geothermal Loop Test Facility (GLEF) which utilizes geothermal fluid from the Salton Sea Field. This paper discusses SDG&E's experience in sampling and analyzing the geothermal fluid flowing through the GLEF.

SAMPLING & ANALYSIS OF GEOTHERMAL BRINES FROM NILAND FIELD, CALIFORNIA

Introduction

The San Diego Gas & Electric Company/U.S. Energy Research and Development Administration Geothermal Loop Experimental Facility (GLEF) located near Niland in the Imperial Valley, California, has operated on a high salinity (200,000 ppm) geothermal fluid from the Salton Sea field since May, 1976. The conversion process being tested is a four-stage/binary system, Figure 1. The geothermal fluid is flashed at successively lower pressures in open drum-type separators. The steam generated passes through a scrubber and into a tube and shell heat exchanger where the heat is transferred to a secondary, working fluid. The working fluid is condensed after expansion across a throttling valve which simulates a turbine. Waste heat is removed via a conventional spray pond. With a turbine generator, to be installed later, this facility would be a 10 MW power plant. Water has been used as the working (binary) fluid during start up and initial operation. Replacement with isobutane, which is expected to be the preferred working fluid for a binary power plant, is planned.

The GLEF has been operated for approximately 2,000 hours with frequent interruption for inspection and facility modification. During this period the facility has been operated on one production well (Magmamax #1). Flow rates were 400,000 pounds per hour, approximately half the design capacity of the GLEF. The temperature and pressure of the fluid entering the first stage is 370°F and 165 psia. Brine exit temperature is 200°F. All unflashed brine is reinjected into the reservoir.

Brine Chemistry

The geothermal fluid available from this reservoir is a hypersaline brine containing approximately 200,000 ppm total dissolved solids (TDS) mostly in the chloride form, Table 1. These chlorides remain in solution during the heat extraction process and are subsequently injected back into the reservoir. Certain minor species, however, such as silica, lead and iron have limited solubility and, as the brine is cooled during the heat extraction process, they precipitate from solution and deposit on pipe and vessel surfaces.

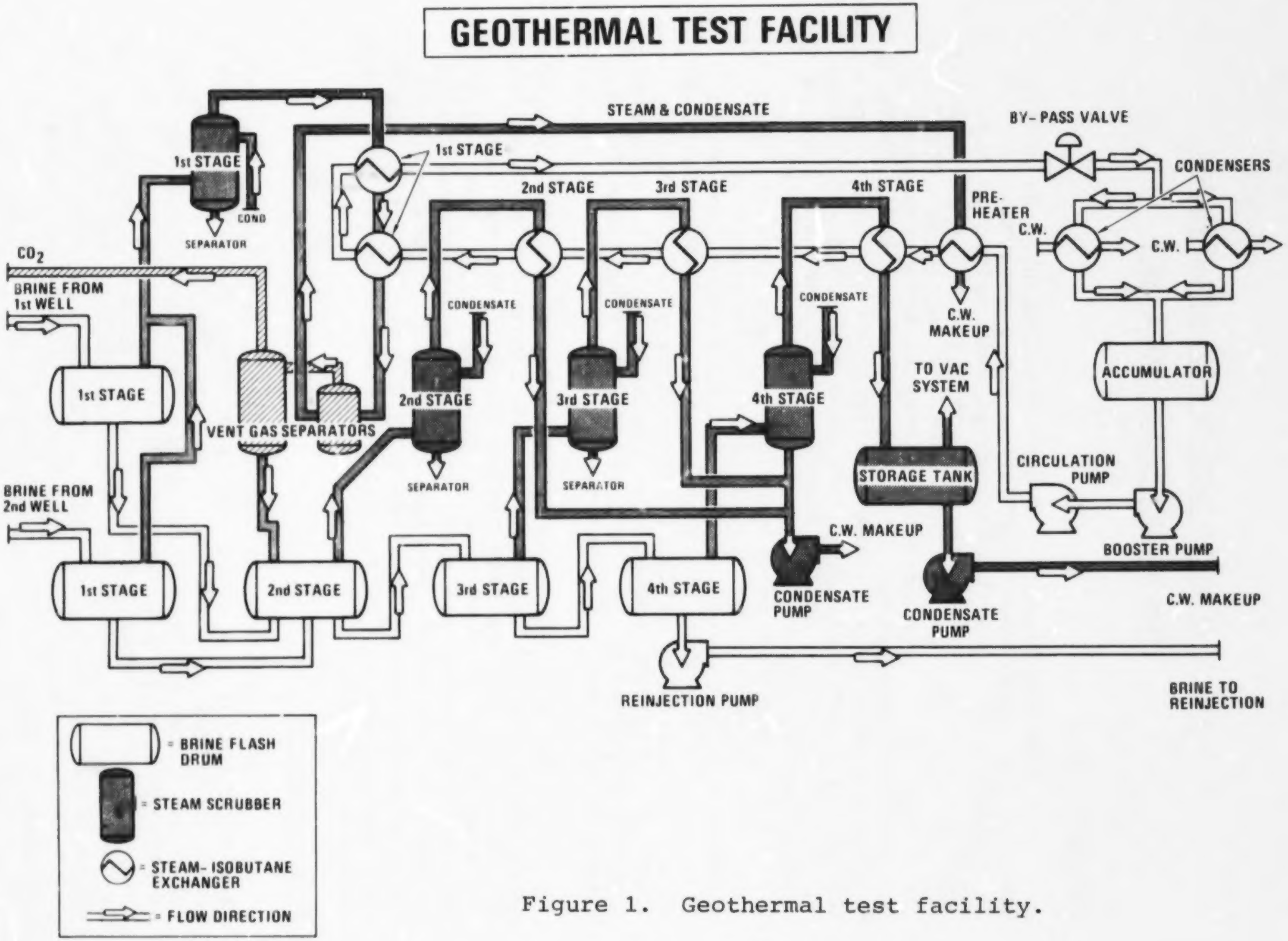
GEOTHERMAL TEST FACILITY
STEAM & CONDENSATE
BY-PASS VALVE
CONDENSERS
1st STAGE
2nd STAGE
3rd STAGE
4th STAGE
PRE-HEATER
C.W.
C.W.
COND
SEPARATOR
CO2
BRINE FROM 1st WELL
BRINE FROM 2nd WELL
CONDENSATE
CONDENSATE
CONDENSATE
C.W. MAKEUP
TO VAC SYSTEM
ACCUMULATOR
1st STAGE
VENT GAS SEPARATORS
2nd STAGE
3rd STAGE
4th STAGE
SEPARATOR
SEPARATOR
STORAGE TANK
CIRCULATION PUMP
C.W. MAKEUP
BOOSTER PUMP
1st STAGE
2nd STAGE
3rd STAGE
4th STAGE
CONDENSATE PUMP
CONDENSATE PUMP
C.W. MAKEUP
REINJECTION PUMP
BRINE TO REINJECTION
= BRINE FLASH DRUM
= STEAM SCRUBBER
= STEAM-ISOBUTANE EXCHANGER
= FLOW DIRECTION

Figure 1. Geothermal test facility.

TABLE I

GEOTHERMAL FLUID COMPOSITION
NILAND RESERVOIR
(MAGMA MAX NO. 1)

ELEMENT	mg/l
Sodium	40,600
Potassium	11,000
Calcium	21,400
Chlorides	128,500
Iron	315
Manganese	681
Zinc	244
Silicon	246
Barium	142
Lead	52
Strontium	440
Lithium	180
Magnesium	105
Copper	3
Ammonia	360
Total Solids	219,000
pH	5.3
Oxidation Reduction Potential	+25

GAS ANALYSIS

ELEMENT	PERCENT
Carbon Dioxide	98.14
Methane	0.68
Nitrogen	0.02
Oxygen	N.D.*
Hydrogen	N.D.*
Hydrogen Sulfide	0.18

*N.D. -- Not Detected

The principal noncondensable gas is carbon dioxide. Small amounts (up to 30 ppm) of hydrogen sulfide are also found in the geothermal brine. Ammonia is also present in the geothermal brine and has a significant effect on the brine chemistry.

Sampling

In order to document the operation of the GLEF and to understand the complex chemistry of the geothermal brines, the brine and steam flows throughout the GLEF are sampled routinely. Sampling is usually accomplished using a glass bottle and a sample cooler. The sample cooler consists of a bundle of 20 stainless steels tubes approximately 4 inches long inside a 2-inch steel pipe. The geothermal fluids pass through the tubes and the cooling water around the outside of the tubes. Generally the samples are taken from near the pipe wall. However, for two phase flow and if suspended solids are to be measured a probe is inserted into the pipe to provide a more representative sample.

Noncondensable gas samples are taken from either the well head or from the first stage heat exchanger, where all steam from the first stage is condensed, utilizing a stainless steel sample bomb. A very simple procedure is used in which the bomb is vented to the atmosphere for approximately 5 minutes to insure equilibrium conditions are established, then the exit valve is closed and followed by the inlet valve trapping a sample of geothermal fluid in the bomb.

Suspended solids develop when the solubility of varied species within the geothermal brine is exceeded during the heat extraction process. These are normally determined using a sample probe and a filter. A known amount of geothermal fluid is withdrawn from the flow with the sample probe and passed through a 10μ filter. Suspended solids present are collected on the filter and are subsequently weighed and analyzed. The sample procedures and results are described elsewhere in this symposium by J. H. Hill, Lawrence Livermore Laboratory.

Analysis

No particularly unusual mineral species appear to be present in the geothermal brines. However, the number of species is very large so that identification can be difficult and interference is a real problem. Presently, two major instruments, an atomic absorption spectrophotometer (AA) and a gas chromatograph have been used to analyze the liquid and vapor phase respectively. Any solids present were put into the solution and analyzed by AA. The method of standard additions is normally used in the AA analysis. Other instruments that have been used successfully include a conductivity bridge, a pH meter and a specific ion electrode for ammonia. Both the conductivity and pH of the fluids were measured at room temperature.

Gas samples were analyzed almost immediately after sampling to reduce any possible reactions in the fluid or with the bomb surfaces. The temperature of the gas sample was also raised to match that of the fluid during sampling. This is particularly important in a liquid-dominated geothermal reservoir where a representative sample of the geothermal fluid will include considerable water. Thus, at room temperature the sample bomb will be almost filled with water which can absorb some of the gases. The noncondensable gases measured can be different then at the temperatures of the geothermal fluid. Returning the temperature of the bomb to that of the geothermal fluid should provide a gas sample representative of the operating pressure and temperature conditions in the facility.

Certain species such as silica although difficult to measure are important because of their contribution to scaling in the geothermal facility. We have found digestions in a Parr bomb followed by AA analysis to be the most accurate method of measuring the silica present in the geothermal brines.

Conclusions

Sampling and analysis of geothermal fluids, particularly the hypersaline brines from the Niland reservoir is difficult. Representative samples must be taken of hot fluids and two phase flow. Sampling procedures must also allow for cooling the fluids in order to conduct analysis without markedly changing fluid properties and to allow for deposition of scale on the sample ports and line. The chemical specie present must be determined in the presence of other species with potential interferring properties. All of this effort must take place under field conditions normally some considerable distance from any well established laboratory. Either a field laboratory must be provided or specimens must be treated so they can be transported without degradation due to storage to such a laboratory.

INTERPRETATION OF ANALYTICAL RESULTS, THERMAL AND NONTHERMAL WATERS, LAVA PLATEAUS REGION OF NORTHEASTERN CALIFORNIA AND SOUTHERN OREGON

C. W. Klein and J. B. Koenig
GeothermEx, Inc.
901 Mendocino Ave.
Berkeley, CA 94707

Abstract

Nonthermal spring and well waters of the Lava Plateaus region (60,000 km^2) are characterized by low TDS (average < 150 μmho/cm) and the weight abundance relationships $Ca > Na \geq Mg > K$ and $HCO_3 + CO_3 >>> SO_4 = Cl$. SiO_2 varies widely, averaging about 25 to 30 mg/l but reaching 50 to 70 mg/l in waters derived from lacustrine sediment or glassy tuff. Evolution of CO_2 gas becomes more notable with increased proximity to the volcanically active High Cascades.

Lakes occupying closed basins in this region show greatly increased TDS. Within the anion group, $HCO_3 + CO_3 >> SO_4 = Cl$ is still common, but certain waters contain SO_4 and sometimes Cl in greater abundance than the carbonate-bicarbonate ions. Major cation concentrations are highly variable; either Na or Ca predominates, and K is usually the least abundant.

Thermal springs and wells show: (1) increased TDS, usually about 500 to 2,000 mg/l; (2) SiO_2 usually less than 100 mg/l but up to 180 mg/l; (3) relative cation weight abundances of Na >> Ca $\geq$ K >> Mg; and (4) relative anion abundances SO_4 > Cl > HCO_3. These relationships are quite typical of nearly all higher temperature waters in the region. In waters sampled at about 50°C or less, the mixes of cations and anions tend to vary, either due to mixing of deep and hot Na-SO_4-Cl waters with shallow, cool Ca-HCO_3 waters or perhaps because of rapid heating and circulation of meteoric waters along fault planes without coming into chemical equilibrium in a deep reservoir. Thermal waters in which chloride is the dominant anion are uncommon throughout the Lava Plateaus region.

Maximum reservoir temperatures indicated by SiO_2 content and an assumption of quartz equilibrium reach about 140°C (= 100 mg/l SiO_2) to 160°C. Na-K-Ca temperatures tend to be lower, perhaps due to continued rock-water interactions during ascent of fluids or because SiO_2 reflects equilibrium with chalcedony or amorphous SiO_2. Na-K-Ca temperatures of mildly thermal and cool waters of the region occasionally are higher than those calculated for the thermal waters.

The uniformity of results across this wide region is notable, as is the relationship of most thermal waters to Quaternary (or Late Tertiary) faults. The data suggest that heating of the waters is most typically caused by circulation to several kilometers along faults in a geothermal gradient of 50° to 60°C/km, with attendant rock-water interaction. We believe that little or no mixing occurs in the region's hotter thermal waters as they rise to the surface, and reservoir temperatures greater than 160°C seem uncommon. If waters exist stored at deeper levels and higher termperatures, they have not been sampled and their composition remains unknown, but saline, Cl-rich compositions may be most likely.

Introduction

Since 1970 GeothermEx, Inc., of Berkeley, California, has carried out on the behalf of numerous clients reconnaissance level and detailed exploration programs in what we will here name the Lava Plateaus region of northeastern California and southern Oregon. This work has included sampling of over 400 hot and cold springs and wells. The results of these analyses, along with some 200 data points published mostly by the USGS, have given us a fairly thorough picture of the major element chemistry of the region's thermal and nonthermal ground waters. It is our intention here to outline some of these observations. Hopefully, they will be useful to others working in the area and to persons seeking to define the possible effect of its geothermal development or regional trends in the character of thermal waters.

The region comprises 60,000 km^2 of volcanic terrane (Figure 1). It is mostly a portion of the Basin and Range structural and geomorphic province, characterized by north- to northwest-trending tilted fault blocks, bounded by steeply-dipping normal faults. The exposed stratigraphic section consists of Tertiary and Quaternary volcanic and sedimentary rocks. The volcanic rocks are basaltic to rhyolitic in composition. Basement, lying at probably 7,000 to over 12,000 feet, is doubtlessly of Mesozoic age. At the west fringe of the area lies the Cascade Range, including in California the areas of Mount Lassen and the Medicine Lake Highland, which have had silicic eruptions in the last 10,000 years.

In the east and northeast, surface hydrology is characterized by internal drainage to shallow, ephemeral lakes. Rivers drain portions of the west. However, the lack of surface waters in some areas is notable. Over many hundreds of square kilometers north of Mount Lassen, for example, there is nearly no surface water to be found. All precipitation percolates down through highly permeable basalt flows, issuing as springs at flow fronts and along fault scarps, sometimes after many miles of travel and in truly astounding volumes.

Average precipitation on the Plateaus region ranges from as little as 8 inches in basins to over 30 inches on higher mountains. The Cascade Range catches most moisture which might otherwise fall on the plateaus, with 50 to 70 inches of annual precipitation falling at higher altitudes.

Ground water is abundant at shallow levels beneath basins, range front fans and landslides, and at variable levels beneath highlands composed of Plio-Pleistocene, highly permeable basalts. These rubbly rocks can act as unconfined aquifers, beneath which the water table is nearly its level in adjacent lake basins. However, sections of older, more weathered basalt and tuff and diatomite are, of course, relatively impermeable. In some basin areas, artesian conditions are common.

Principal thermal springs and wells typically issue along range-front faults or are believed to be associated with major faults, on the basis of geologic mapping and geophysical studies. Deep circulation along faults is thus the probable mechanism of heating except at Mount Lassen and the Medicine Lake Highland, where magmatic heat sources undoubtedly exist. No evidence for shallow magmatic sources elsewhere has thus far been encountered.

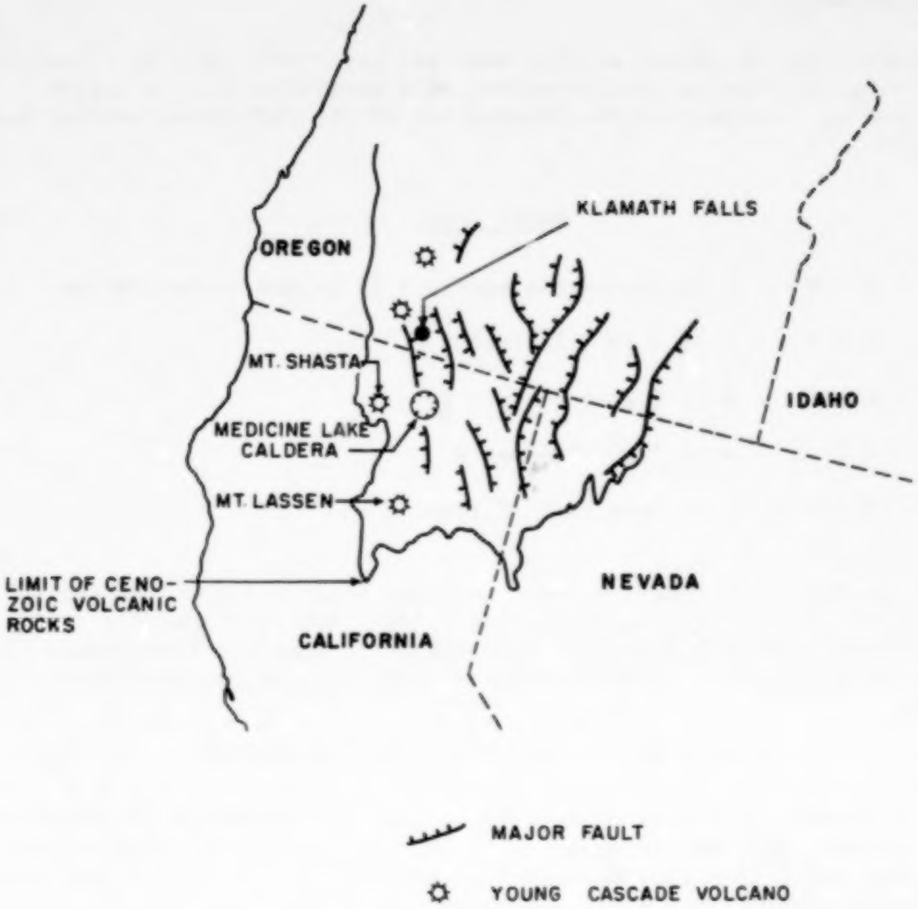
KLAMATH FALLS
OREGON
MT. SHASTA
IDAHO
MEDICINE LAKE
CALDERA
MT. LASSEN
LIMIT OF CENO-
ZOIC VOLCANIC
ROCKS
NEVADA
CALIFORNIA
MAJOR FAULT
YOUNG CASCADE VOLCANO

Figure 1. Sketch map showing the lava plateaus region.

Hydrochemistry

In discussing the ground waters, chemical types will here be illustrated according to relative concentrations on a *weight* basis in a system employed by Truesdell in the Proceedings of the 1975 UN Geothermal Symposium:

Water Type

A = B --- A approximately equals B in *weight* concentration

A $^{>}$ B --- A is 1 to 1.2 times B

A > B --- A is 1.2 to 3 times B

A >> B -- A is 3 to 10 times B

A >>> B - A is more than 10 times B

Cold springs, upland well waters, and some basin wells of the region are characterized by low total dissolved solids (TDS) and specific conductance (SpC). TDS averages less than 150 mg/l, specific conductance less than 150 micromhos. Weight abundance relationships are typically:

$$\mathrm{Ca} > \mathrm{Na} \geq \mathrm{Mg} > \mathrm{K} \text{ and } \mathrm{HCO_3} + \mathrm{CO_3} >>> \mathrm{SO_4} = \mathrm{Cl}$$

CO_3 is rarely present as pH is usually near 7. Cl and SO_4 are each less than 2 mg/l, and HCO_3 is about 30 to 100 mg. With rare exceptions Ca is the most and K the least concentrated cation. Na is usually more concentrated than Mg, but there are exceptions where these two ions are about equally concentrated, and occasionally Mg is the more abundant. SiO_2 varies widely, averaging about 25 to 30 mg/l but reaching 50 to 70. These higher levels are sometimes seen in nonthermal well waters derived from lacustrine sediments or glassy tuff, where silica solubility may be controlled by amorphous silica more than quartz. Very rarely, we have seen SiO_2 as high as about 120 mg/l in cold springs far from known thermal areas and which otherwise display no traces of possible thermal effects or other anomalies. Where we have applied the Na-K-Ca geothermometer to the cold waters, the resulting temperatures calculated are usually low, as would be expected. However, about one water sample in 15 or 20 gives a temperature which is abnormally high. We suspect that this is caused by circulation of such waters through rocks or mineral zones from which potassium is easily leached.

Ground waters in the lake basins commonly show slightly to greatly increased TDS, to over 1,000 mg/l. The types of water become somewhat variable; either Na or Ca predominates the cations, and K is usually the least abundant. Within the anion group, bicarbonate is still the most abundant species, and rough equivalence of SO_4 and Cl is still common. However, certain waters contain SO_4 and sometimes Cl in greater abundance than the carbonate-bicarbonate ions. These variable compositions doubtlessly reflect mixing of such factors as changing sediment composition, local concentrations of somewhat saline pore fluids, and lateral migration of meteoric waters into the basin aquifers.

Thermal springs and wells are of fairly uniform character throughout the region. Typically:

$$\text{Na} \gg \text{ to } \ggg \text{Ca} \geq \text{K} \gg \text{Mg and}$$

$$SO_4 > \text{ to } \gg \text{Cl} > \text{ to } \gg HCO_3$$

TDS are usually about 500 to 2,000 mg/l. Amongst the cations, Na is characteristically dominant. Ca is greater than K and Mg the least concentrated. Although usually Ca $\geq$ K, the relative abundancies vary from $\geq$ to >>, and between K and Mg we have seen K > Mg to K >>> Mg. Anion analyses most frequently show that SO_4 is more concentrated than Cl, and bicarbonate is the least abundant. These relationships are quite typical of nearly all the higher temperature waters. At about 50°C or less, the mixes of cations and anions tend to vary. TDS are low, and we occasionally see Ca > Na and HCO_3 as the dominant anion. This is perhaps due to mixing of deep and hot $Na\text{-}SO_4\text{-}Cl$ waters with shallow, cool $Ca\text{-}HCO_3$ waters or because of rapid heating and circulation of meteoric waters along fault planes without coming into equilibrium in a deep reservoir. Thermal waters in which chloride is the most abundant anion are very uncommon throughout the region.

SiO_2 in the thermal waters is usually less than 100 mg/l but occasionally is seen to 180 mg in springs above about 80°C. The 100-mg level indicates a quartz equilibrium temperature of 140°C. Na-K-Ca temperatures tend to fall below the quartz temperatures by about 10° or 20°C, perhaps due to reequilibration upon cooling; some cation temperatures are higher and some are a good deal lower than the quartz values. This suggests possible equilibrium with cristobalite or chalcedony, as has been pointed out also by Mariner and others and by Reed in studies of parts of the same region.

Interpretations

The uniformity of hot spring compositions across this wide region is notable, we think; in particular, as they are usually characterized by relatively low total dissolved solids compared with hot springs worldwide and dominance of the anions by SO_4 instead of Cl or HCO_3. If we move westward into the Cascades either in Oregon or at Mount Lassen in California, higher TDS to over 4,000 mg/l are common, and Cl is very dominant. In the Basin and Range province in Nevada, reported TDS tend to be near or above 2,000 mg/l, with HCO_3 or Cl the most abundant anion.

Relative absence of chloride and low TDS in the hot springs may be caused by several conditions, none of which are certain. These include: low aquifer temperatures, short residence time, the effects of rock composition, and dilution of deep, very hot chlorided waters by meteoric waters during travel to the surface.

Although the presence of deep, hot, chloride-rich aquifers can be imagined, evidence of their existence has not been seen, either in surface waters or in the few deep tests which have been drilled.

Rock composition is a factor which is hard to evaluate without petrochemical studies. We don't know the relative amounts of SO_4 and Cl which hot waters can leach from igneous rocks of the area. Some SO_4 may originate in basin sediments, with which most of the thermal springs are associated.

By comparison, note the correlation between relatively low chloride and the absence of either basement rocks or andesitic volcanics from the region. Chloride is the characteristic anion of hot springs not only in the Cascades but also in the andesitic chains of Central America. Basement rocks are usually in the vicinity of hot springs in Nevada, in which SO_4 is rarely the most abundant anionic species.

Some workers have suggested that where aquifer rocks do not include sources of a particular anion in abundance, such as evaporites, the dominant anion of a hot spring *may* be related to its relative maturity or residence time. Thus, bicarbonate waters are youthful while sulfate waters are of intermediate and chloride waters of most advanced age. The Plateaus hot springs would thus be classified as intermediate. The relatively low apparent aquifer temperatures would be consistent with this, and both could be controlled by relatively rapid circulation of the waters to a limited depth down and back up along fault zones. Water could heat to a reservoir temperature of 130°C by circulation to only

4,300 m down a 30°C/km gradient. This depth is very roughly where we expect the top of Mesozoic basement, so the waters may experience at most a brief residence in basement rocks. Exploration experience at some springs suggests localization of heated waters along fault planes or at least an absence of extensive hot aquifers easily tapped by deep drilling. However, the thermal aquifer at Klamath Falls is apparently quite large and may store water for a considerable period of time.

We are, by the way, gratified to see that Ed Sammel and co-workers at the USGS have reached conclusions about the Klamath Falls geothermal system which are essentially similar to our own.

In conclusion, the uniformity of composition across this wide region and generally good agreement between the silica and cation geothermometers suggest that little or no mixing occurs in its hotter thermal waters as they rise to the surface. Reservoir temperatures greater than 130° to 160°C seem uncommon. We seem to be seeing in the plateaus region an example of an extensive geothermal province of uniform chemical character.

It may be possible to similarly outline other geothermal provinces within which expectable ranges of effluent composition can be constrained to limits useful in modeling the possible environmental effects of development.

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ABSTRACT

GEOCHEMICAL ANALYSIS OF FLUIDS CIRCULATED THROUGH A GRANITIC HOT DRY ROCK GEOTHERMAL SYSTEM

J. W. Tester, C. Grigsby, C. Holley, and L. Blatz
Los Alamos Scientific Laboratory
University of California
Los Alamos, New Mexico

Results of preliminary field tests involving circulating filtered water through a hydraulically fractured geothermal reservoir composed of granite at 200°C are reported. The reservoir is connected to the surface by two approximately 10,000 ft (3 km) holes, used for injection and recovery fluid. Chemical composition of the fluid samples was monitored at the site using spectrophotometric and specific ion electrode techniques. Supplemental measurements were made at our central laboratory facility using neutron activation, emission spectroscopy, and atomic absorption. The major cations and anions in a fluid specimen that had circulated through the fractured granitic system for a mean residence time of 10 hrs would include:

> SiO_2 (180-260 ppm), Na (400-750 ppm), K (400-650 ppm), Ca (2-10 ppm), Mg (1-3 ppm), Al (<1 ppm), Fe (2-3 ppm), Mn (∿0.01 ppm), Cl (400-600 ppm), F (12-14 ppm), HCO_3 (150-200 ppm), PO_4 (0.1-0.2 ppm), and pH (6.8-7.0).

With fresh water injection a steady state exiting fluid composition is reached within 10 hrs indicating a rapid rate of dissolution mass transport between the rock surface and injected fluid. Of the major components only the fluoride levels of 12-14 ppm present a possible environmental hazard. Trace element analysis indicated that levels of other toxic elements were below EPA recommended levels for continuous irrigation or livestock feeding. Because complete recirculation (or reinjection) of fluid will be primarily used in the present hot dry rock demonstration system after the temperature has been reduced with an air-cooled heat exchanger, only periodic treatment of a part of the water may be required to remove fluoride. Organic dyes have been periodically injected into the system for tracer analysis of residence time distribution. Both activated charcoal and activated alumina have been investigated in field and laboratory experiments to determine their fluoride and dye removal efficiencies. Experiments showed that fluoride levels would be reduced to <0.1 ppm with a properly activated alumina bed. Silica was also removed quite effectively. As expected, the activated charcoal removed up to 20 ppm of dye to below the detection level of our spectrophotometric technique (0.05 ppm).

ABSTRACT

CHEMICAL PROFILE OF THE EAST MESA GEOTHERMAL FIELD, IMPERIAL COUNTY, CALIFORNIA

R. T. Littleton and E. Burnett
U.S. Bureau of Reclamation, Boulder City, Nevada

The East Mesa Geothermal Field, about 18 miles east of El Centro, California, is a thermal knot in saturated deltaic and lacustrine sediments. A deep convective system drives geothermal fluids through a reservoir of interconnected lenses of sand and sandstone throughout a depth interval of about 4,500 feet between about 7,500 and 3,000 feet.

A gross evaluation of the geochemical profile of the reservoir is attempted by interpretation of the resistivity and self-potential curves of the dual induction log. The geochemical profile shows a typical pattern throughout the reservoir. Typically, salinity increases with depth reaching a maximum between 2,000 and 3,000 feet, then decreasing to about 6,000 feet, and then increasing sharply to a depth of about 7,500 feet. Below 7,500 feet we are unable to compute salinities with confidence and our reasons are discussed.

The shape and dimensions of the geothermal field in relation to depth are discussed. Chemical profiles are computed from dual induction logs of 10 geothermal wells in and around the East Mesa Geothermal Field and related to laboratory analysis of fluids recovered from drill stem tests and produced at the wellhead. The relation of the geochemical profiles to the movement of geothermal fluids in the reservoir is discussed.

CHEMICAL PROFILE
OF THE EAST MESA FIELD
IMPERIAL COUNTY, CALIFORNIA

by
Robert T. Littleton and Earl E. Burnett
U. S. Bureau of Reclamation
Lower Colorado Region

February 1977

INTRODUCTION

The East Mesa Geothermal Field is about 18 miles east of El Centro in Imperial Valley, California. Exploration and evaluation of temperature gradients, gravity responses, and resistivity measurements by Robert W. Rex and his colleagues at the University of California at Riverside, largely supported by Reclamation funds, led to the discovery of the field. The dimensions of the field are beginning to emerge as the result of drilling by Reclamation, Magma Energy Company, and Republic Geothermal Incorporated.

This paper was prepared by the authors largely on the basis of interpretations from the dual induction resistivity logs of 10 geothermal deep wells and laboratory analyses of water samples of 5 geothermal deep wells.

The authors express their appreciation to Reclamation's Regional Director, Manuel Lopez, Jr., and Regional Planning Officer, M. K. Fulcher for support in these studies. The authors also appreciate the generosity of Mr. W. C. McCabe of Magma Energy Company and Robert W. Rex of Republic Geothermal Incorporated for releasing geophysical logs of geothermal deep wells.

THERMAL DIMENSIONS OF THE GEOTHERMAL FIELD

The East Mesa Geothermal Field apparently is a thermal knot in saturated deltaic and lacustrine sediments. A deep convective system drives geothermal fluids through a reservoir of interconnected and faulted lenses of sand and sandstone throughout a depth interval between 3,000 and 7,500 feet. About 70 percent of this interval is sand and sandstone creating a reservoir of roughly 3,150 feet of lenticular permeable beds interconnected to various degrees, due partly to stratigraphic interfingering but largely by transecting faults.

Isothermal contouring based upon equilibrium temperature profiles in 10 geothermal deep wells (Figures 1 through 4) suggest the dimensions of the geothermal reservoir. When considered together, the four different isothermal maps indicate the shape of a geothermal plume rising into a cold ground water reservoir. The plume is bent north-northwest from an apparent geothermal center in about the NE¼ of sec. 7, T. 16 S., R. 17 E., SBM, following avenues of permeability established by the stratigraphic makeup of the reservoir but also by transecting faults.

GEOCHEMICAL PROFILE OF THE RESERVOIR

General Considerations

A gross evaluation of the chemical profile of the reservoir is made by interpretation of the resistivity and self-potential curves of the dual induction logs. The chemical profiles are shown as total dissolved solids which is estimated from the computed electrical conductivity. Chemical profiles were computed for 10 geothermal deep wells (see Figures 5 through 7). The method used to calculate the electrical conductivity of fluid in the reservoir is fairly well known. It is based upon formulae and methodology discussed in text books such as Sylvain T. Pirson's Handbook of Well Log Analysis (Prentice Hall, 1963) and Service Company Manuals by Schlumberger Well Surveying Corporation. The chemical profile computed is for salinity only, as indicated by the concentrations of sodium and chloride ions.

Computer Program

The computer program has been developed to calculate the electrical conductivity of formation water from a suitable set of resistivity and self-potential curves. The methodology requires an accurate measure of the mud filtrate resistivity at 77°F. To convert the mud filtrate resistivity ($Rmft_1$) at some temperature t_1 to 77°, we use the following formula:

$$Rmf_{77} = (Rmft_1)(t_1/77)$$

where t_1 = fahrenheit temperature

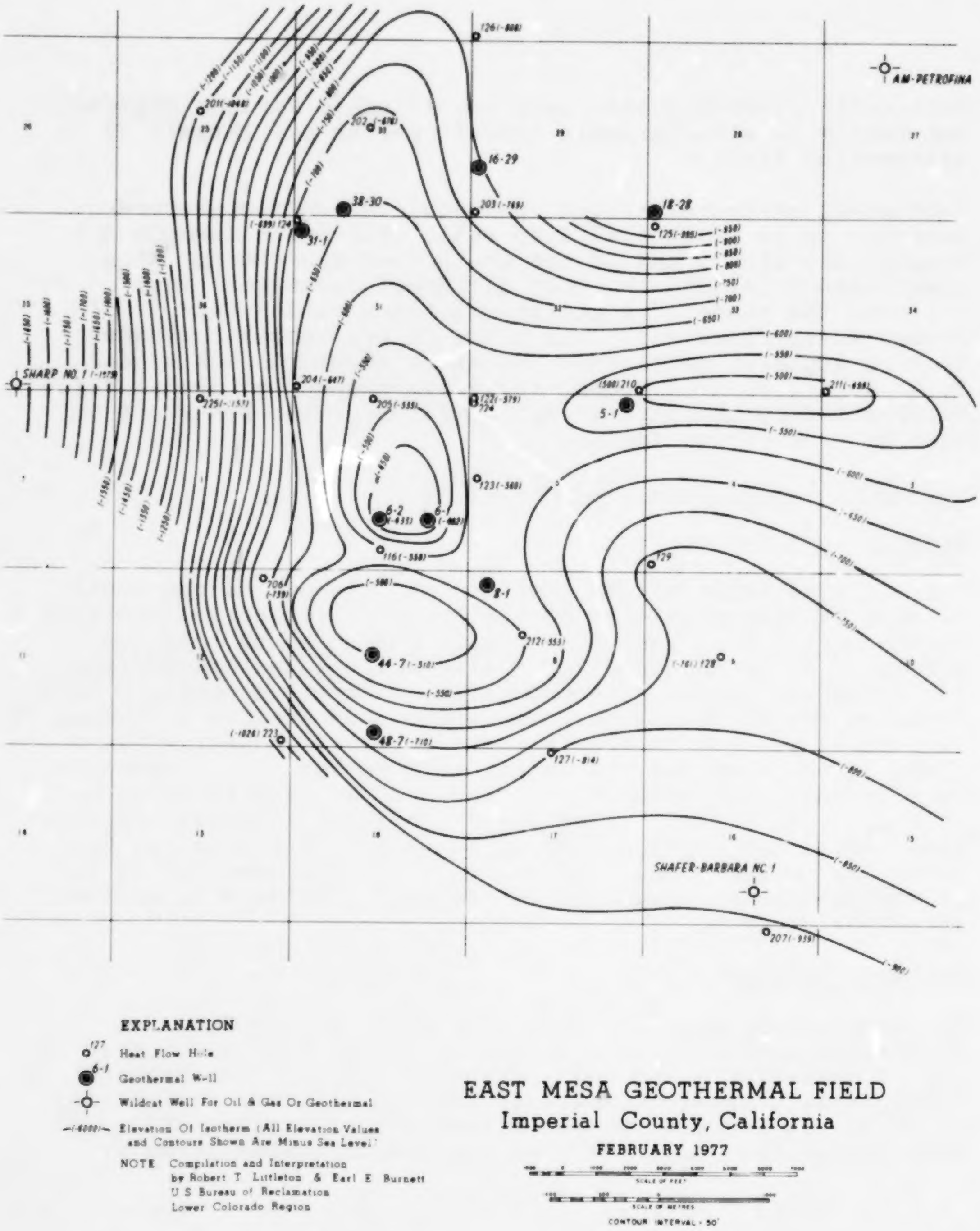

AM-PETROFINA
SHARP NO. 1
SHAFER-BARBARA NO. 1
16-29
18-28
38-30
31-1
5-1
6-2
6-1
8-1
44-7
48-7
126(-808)
201(-848)
202(-678)
203(-769)
125(-885)
204(-647)
225(-751)
205(-555)
222(-579)
123(-560)
116(-558)
206(-759)
212(-553)
129
128
223
127(-814)
207(-939)
210
211(-498)
(-550)
(-600)
(-650)
(-700)
(-750)
(-800)
(-850)
(-900)
(-950)
EXPLANATION
Heat Flow Hole
Geothermal Well
Wildcat Well For Oil & Gas Or Geothermal
Elevation Of Isotherm (All Elevation Values and Contours Shown Are Minus Sea Level)
NOTE Compilation and Interpretation by Robert T. Littleton & Earl E. Burnett U.S. Bureau of Reclamation Lower Colorado Region
EAST MESA GEOTHERMAL FIELD
Imperial County, California
FEBRUARY 1977
SCALE OF FEET
SCALE OF METRES
CONTOUR INTERVAL = 50'

Figure 1. 150°F isotherm subsurface contour map.

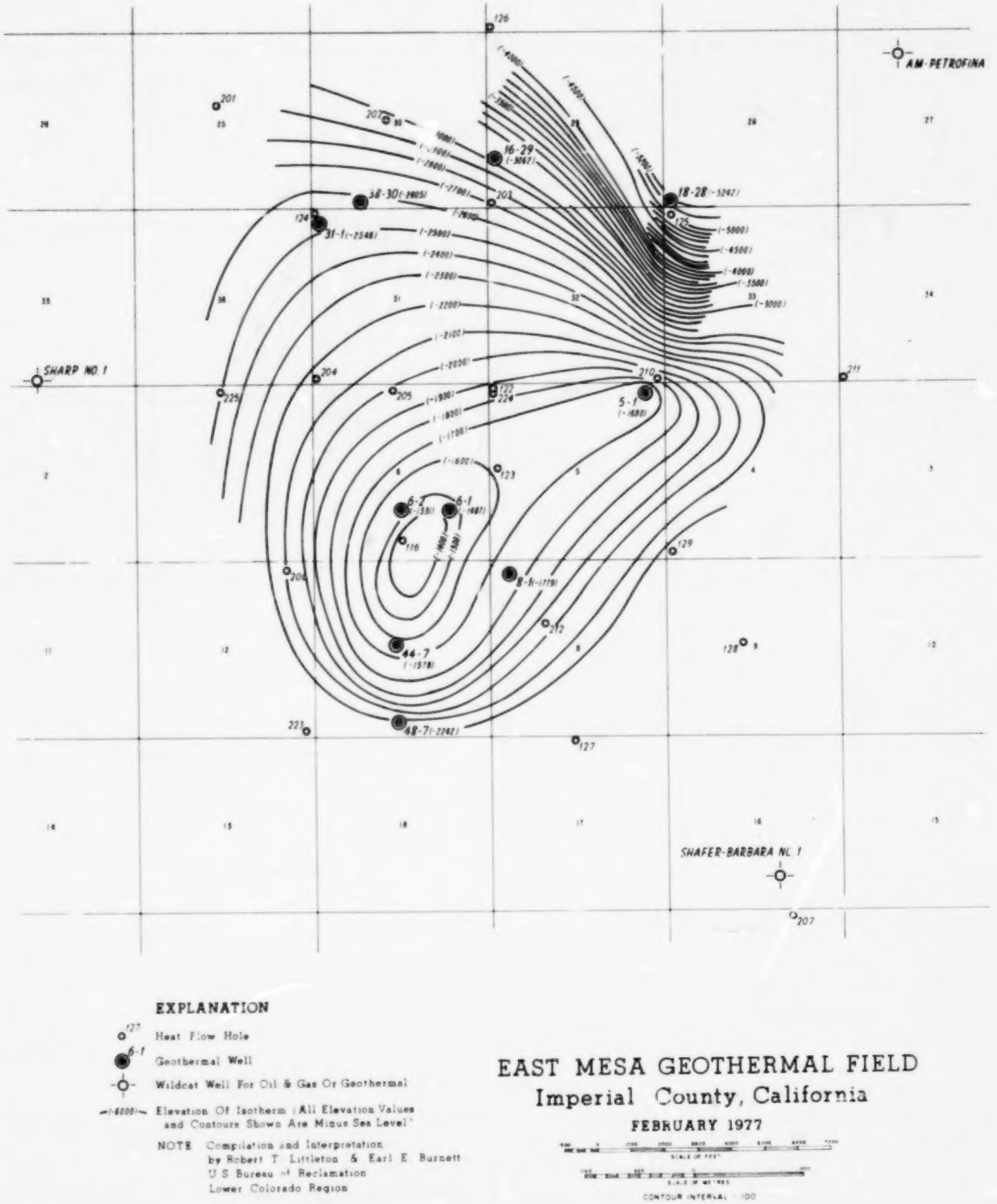
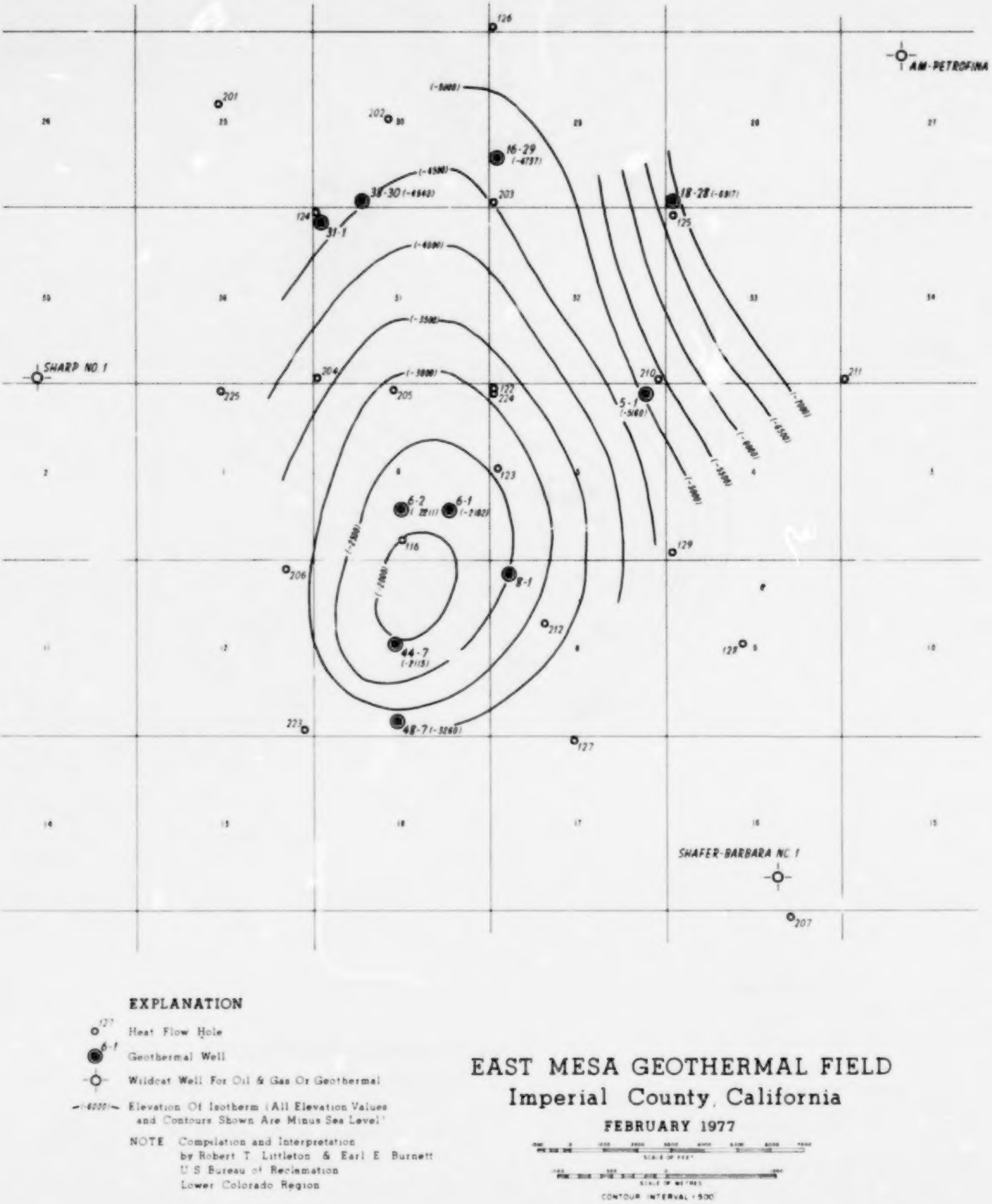

AM-PETROFINA
SHARP NO. 1
SHAFER-BARBARA NO. 1
16-29 (-3062)
18-28 (-5242)
38-30 (-2805)
31-1 (-2549)
5-1 (-1680)
6-2
6-1
8-1 (-1779)
44-7 (-1578)
48-7 (-2242)
EXPLANATION
Heat Flow Hole
Geothermal Well
Wildcat Well For Oil & Gas Or Geothermal
Elevation Of Isotherm (All Elevation Values and Contours Shown Are Minus Sea Level)
NOTE Compilation and Interpretation by Robert T. Littleton & Earl E. Burnett U.S. Bureau of Reclamation Lower Colorado Region
EAST MESA GEOTHERMAL FIELD
Imperial County, California
FEBRUARY 1977
SCALE OF FEET
SCALE OF METERS
CONTOUR INTERVAL 100

Figure 2. 250°F isotherm subsurface contour map.



126
AM-PETROFINA
201
202
(-5000)
16-29
(-4737)
(-4500)
38-30 (-4540)
18-28 (-6917)
203
124
31-1
125
(-4000)
(-3500)
SHARP NO. 1
204
225
(-3000)
205
122
224
210
211
5-1
(-5160)
(-7000)
(-6500)
(-6000)
(-5500)
(-5000)
123
6-2
(-2211)
6-1
(-2102)
(-2500)
(-2000)
116
129
206
8-1
212
128
44-7
(-2115)
223
48-7 (-3260)
127
SHAFER-BARBARA NO. 1
207
26
25
30
29
28
27
35
36
31
32
33
34
2
1
6
5
4
3
11
12
7
8
9
10
14
13
18
17
16
15
EXPLANATION
Heat Flow Hole
Geothermal Well
Wildcat Well For Oil & Gas Or Geothermal
Elevation Of Isotherm (All Elevation Values and Contours Shown Are Minus Sea Level)
NOTE Compilation and Interpretation by Robert T. Littleton & Earl E. Burnett U.S. Bureau of Reclamation Lower Colorado Region
EAST MESA GEOTHERMAL FIELD
Imperial County, California
FEBRUARY 1977
SCALE OF FEET
SCALE OF METRES
CONTOUR INTERVAL 500

Figure 3. 300°F isotherm subsurface contour map.

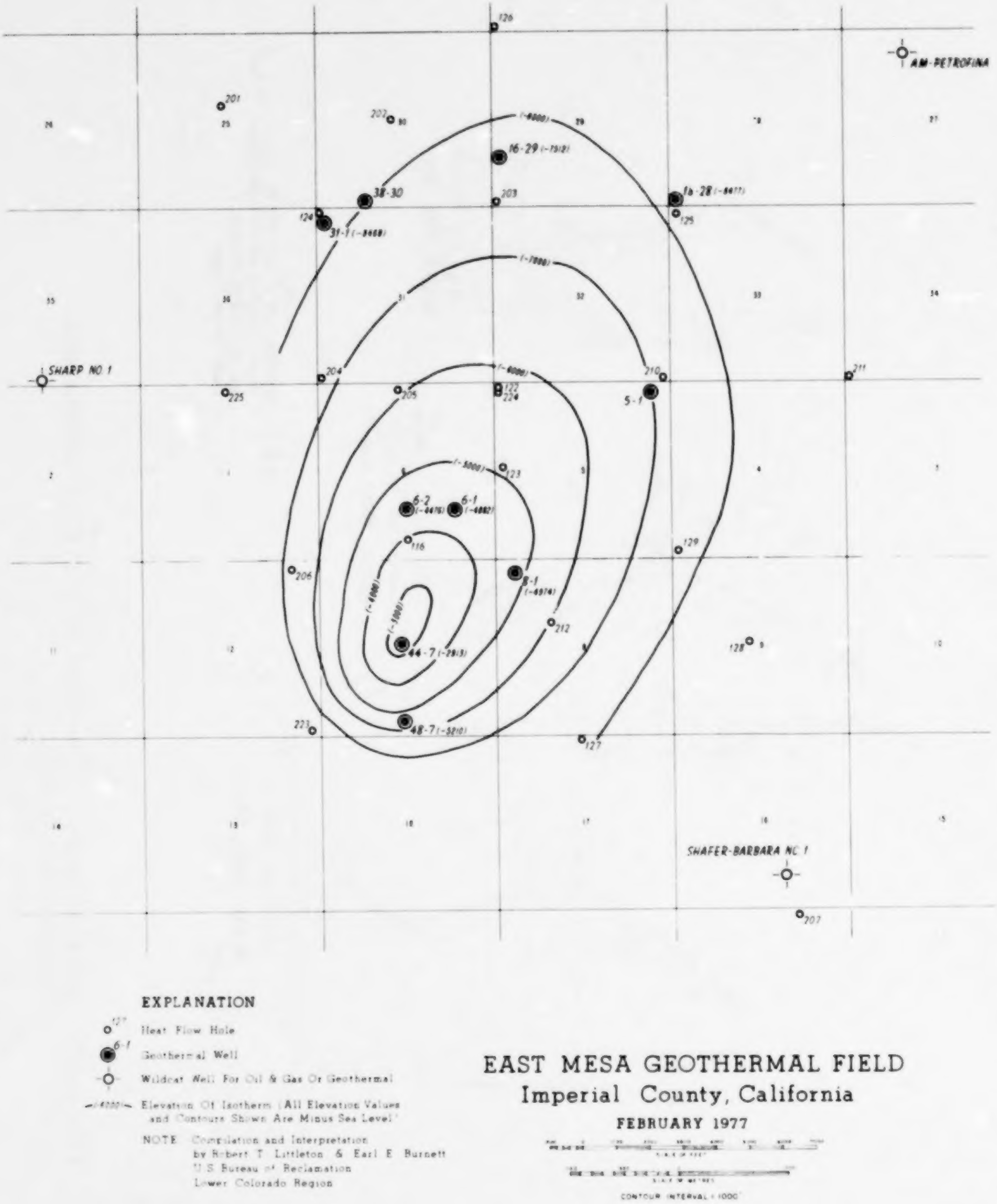
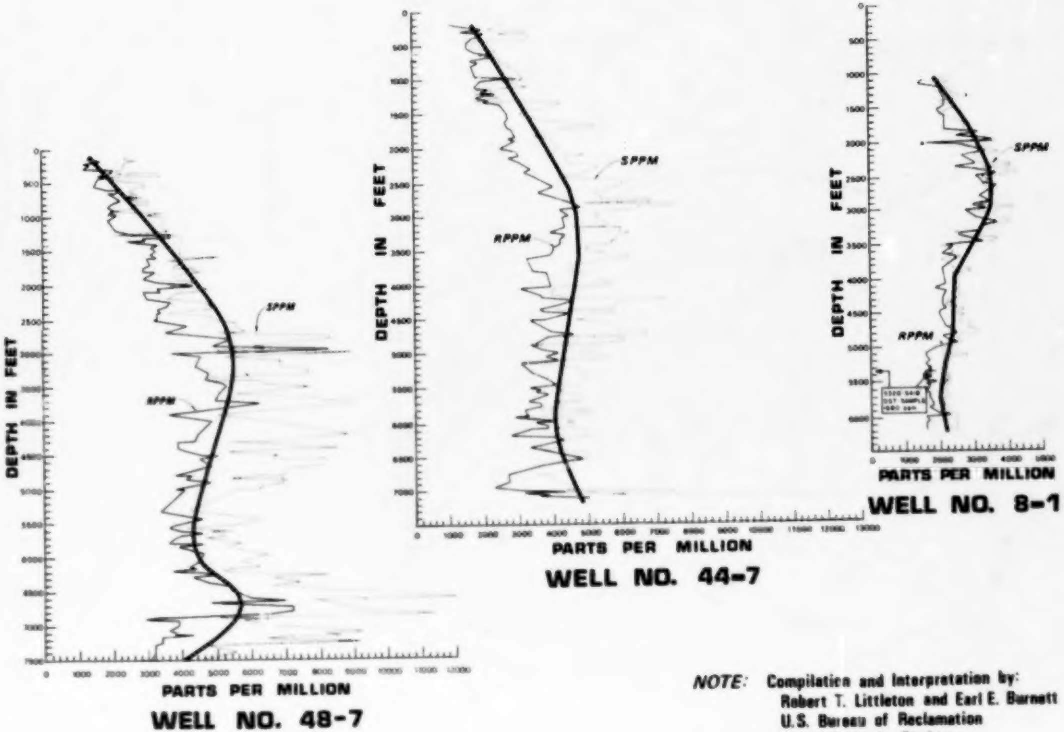
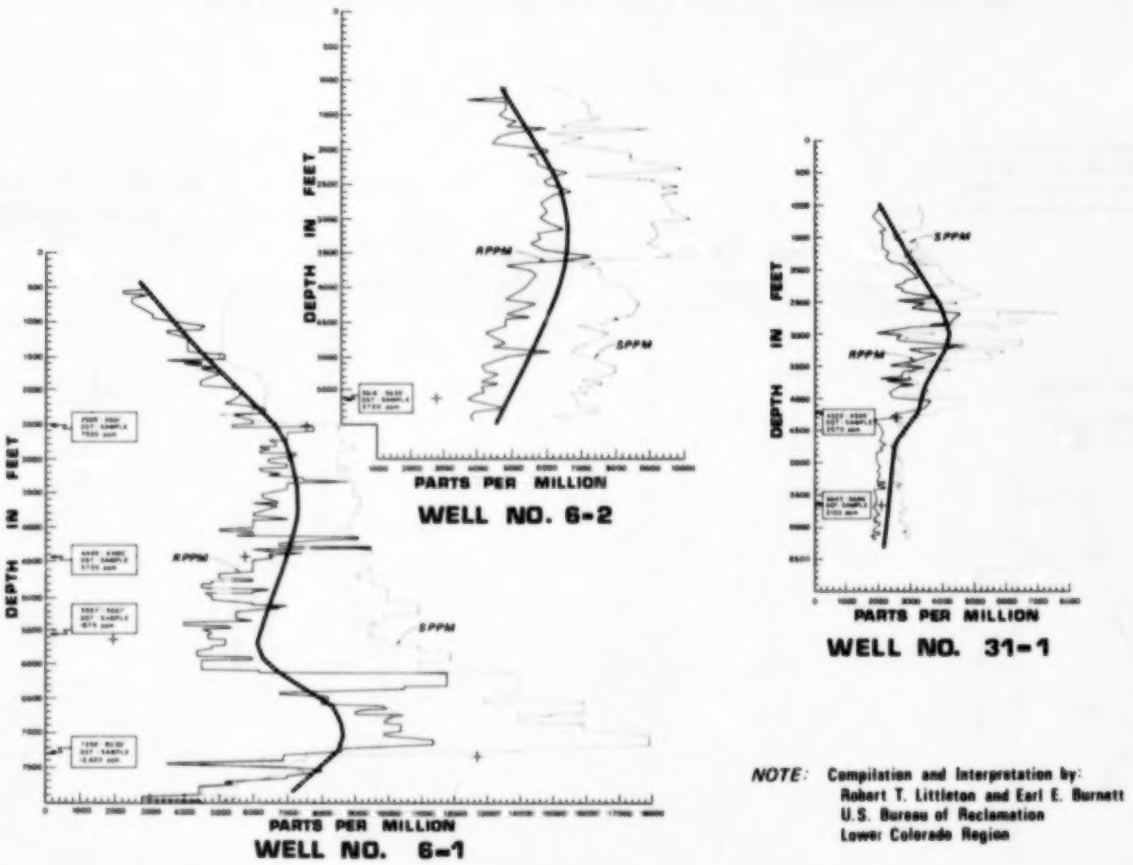

AM-PETROFINA
SHARP NO 1
SHAFER-BARBARA NO 1
16-29 (-7512)
38-30
31-1 (-8468)
16-28 (-8477)
(-8000)
(-7000)
(-6000)
(-5000)
(-4000)
(-3000)
5-1
6-2 (-4476)
6-1 (-4882)
8-1 (-4974)
44-7 (-2915)
48-7 (-5210)
126
201
202
203
204
205
206
122
224
123
116
124
125
127
128
129
210
211
212
223
225
207
EXPLANATION
Heat Flow Hole
Geothermal Well
Wildcat Well For Oil & Gas Or Geothermal
Elevation Of Isotherm (All Elevation Values and Contours Shown Are Minus Sea Level)
NOTE Compilation and Interpretation by Robert T. Littleton & Earl E. Burnett U.S. Bureau of Reclamation Lower Colorado Region
EAST MESA GEOTHERMAL FIELD
Imperial County, California
FEBRUARY 1977
CONTOUR INTERVAL 1000'

Figure 4. 350°F isotherm subsurface contour map.



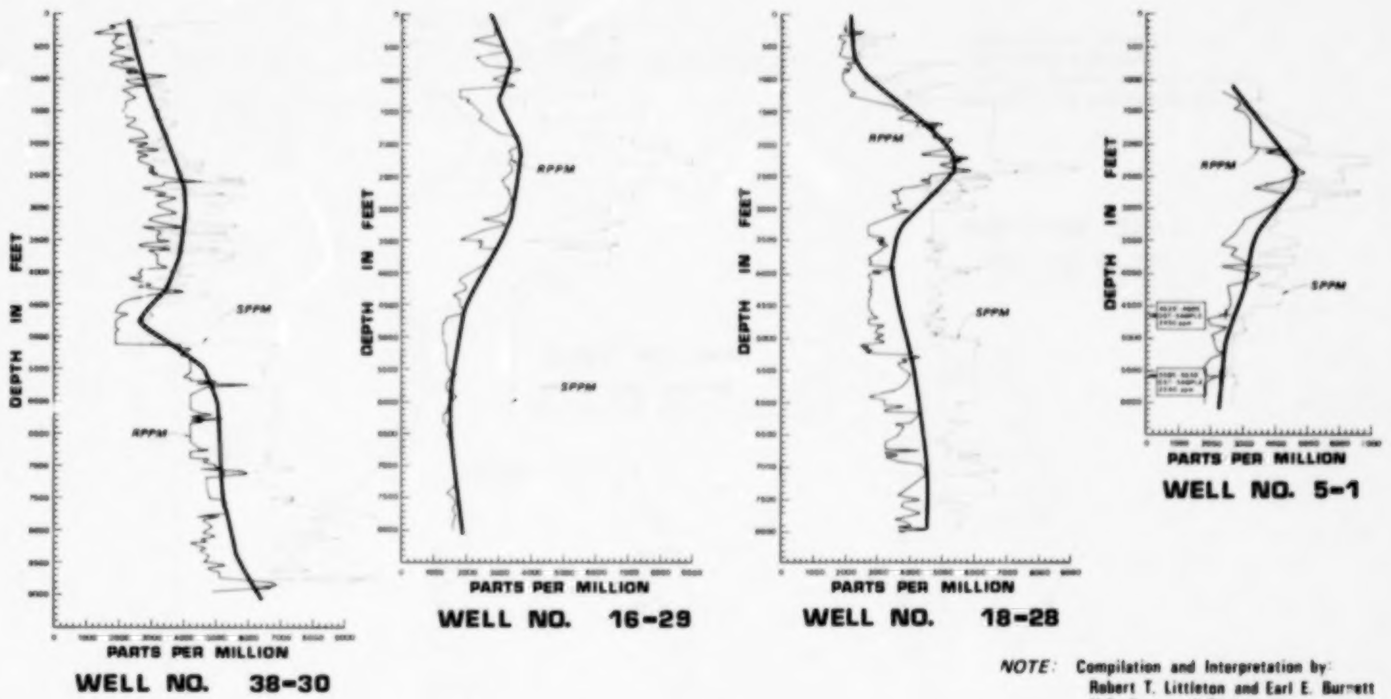
NOTE: Compilation and Interpretation by:
Robert T. Littleton and Earl E. Burnett
U.S. Bureau of Reclamation
Lower Colorado Region

Figure 5. Mesa anomaly. Chemical profile of geothermal wells. (continued)



NOTE: Compilation and Interpretation by:
Robert T. Littleton and Earl E. Burnett
U.S. Bureau of Reclamation
Lower Colorado Region

Figure 6. Mesa anomaly. Chemical profile of geothermal wells. (continued)



NOTE: Compilation and Interpretation by:
Robert T. Littleton and Earl E. Burnett
U.S. Bureau of Reclamation
Lower Colorado Region

Figure 7. Mesa anomaly. Chemical profile of geothermal wells.

Formation temperature at a given depth *is* required to compute salinity from the SP curve but is *not* required to compute salinity from resistivity curves. A measure of geothermal gradient existing during logging is used to estimate formation temperature at any given depth. The following formula is used:

$$t_f = t_s + (G)(D)$$

where t_f = formation temperature in ^{o}F

t_s = temperature of drilling fluid near surface in ^{o}F

$G = \frac{(\text{BHT - SURF. Temp})}{(\text{TD - SURF. Depth})}$ Geothermal gradient as indicated by the bottom hole temperature (BHT) when logged and the surface temperature. Surface temperature should be measured about 50 feet below land surface to avoid surface cooling.

D = depth of formation in feet.

TD = total depth of hole.

Values of resistivity are taken from two curves representing the mud-invaded zone resistivity (shallow induction curve) and the uninvaded zone resistivity (deep induction curve). SP values are a measure of static SP deflection from the shale line. The computer program described in this paper was devised for use in a Texas Instruments SR-52 card programmable calculator. The program can be adjusted to other programmable calculators. A FORTRAN version also exists. The SR-52 program is given in Appendix 1.

The methodology used here can give misleading results due to invasion of mud filtrate water into the permeable formation. The authors believe that such invasion is minimal in saturated formations having solely or primarily intergranular permeability. Laboratory analysis of fluid recovered on drill stem tests independently corroborate the mineral concentration obtained from the resistivity curves of the log. The depth and total dissolved solids of the five Bureau of Reclamation wells are shown by a "+" on Figures 5 and 6 . Two lines of evidence support the contention that formation water is recovered. Near equilibrium formation temperature is achieved during a short test indicating considerable flushing. Further corroboration is by several thousand feet of water column trapped in the drill pipe within a matter of 15 minutes. After about 15 minutes the tool plugs with sand and the test is essentially over.

Conversely reliable results are not obtained in the reservoir with substantial or total fracture permeability. Mud invasion is apparently excessive and deep and the program measures the salinity of the mud primarily.

Characteristics of the Chemical Profile

The general shape of the chemical profile is depicted in Figures 5 and 6 by drawing a heavy line more or less along the trend of resistivity values for each permeable bed. Wells in the central part of the field, i.e., 6-1, 6-2, 44-7, and 48-7 show a broad buildup of chemical concentration between depths of 1,500 and 3,500 feet. The critical reversal points are usually between 2,000 and 3,000 feet depth. A reversal from lower to higher mineralization occurs in most of the wells at depths between 5,700 and 6,900 feet except in Well 38-30 where the depth is about 4,700 feet.

CONCLUSIONS

With adequate dual induction logs, it is possible to estimate the chemical concentration in the intergranular reservoir of the East Mesa Geothermal Field. The chemical concentration in the fractured reservoir cannot be reliably determined because of deep invasion by the drilling mud.

REFERENCES

Pirson, S.T., 1963, Handbook of Well Log Analysis, Prentice Hall, New York, New York.

Schlumberger Well Surveying Corporation, 1972, Log Interpretation Volume I - Principles, Schlumberger Limited, 277 Park Avenue, New York, New York.

Schlumberger Well Surveying Corporation, 1974, Log Interpretation Volume II - Application, Schlumberger Limited, 277 Park Avenue, New York, New York.

APPENDIX 1

An SR-52 Program for Computing Water Salinity Concentrations from Resistivity and Self-Potential Logs

Memory Register Initialization

R01	Mud Filtrate Resistivity at 77°F (ohm-meters)
R02	6000, a constant
R05	2.15, a constant
R06	Drilling mud temperature near land surface, °F
R08	Geothermal Gradient, °F/foot
R09	0.62, empirical constant to convert electrical conductivity to ppm.
R13	70.7, a constant
R14	11764.74, a constant; may be adjusted for a particular ground water reservoir

Other Memory Used

R00	F, formation factor
R10	Ø, Humble formula porosity
R11	m, cementation factor
R12	ppm

Instructions

Initialize memory registers, press CLR, press A, key in depth in feet, press RUN, key in the invaded zone resistivity, Rxo, for that depth, press RUN, read F, press RUN, read Ø, press RUN, read m, press RUN, key in the uninvaded zone resistivity, Ro, for that depth, press RUN, read resistivity log ppm.

For the SP log water quality, press B, key in depth, press RUN, key in static SP deflection, SSP, in negative millivolts, press RUN, read the sp log ppm. For the next sand body press A and repeat the process. If no SP log is available, do not press B but proceed to a new depth by first pressing A and continue as above. If only an SP log is available, begin by first pressing CLR, then press B and continue as above for the SP log and proceed to a new depth by again pressing B, etc. In other words, LABEL A is for resistivity logs and LABEL B is for SP logs and work independently of one another. Of course, the pertinent memory initialization (for RMF_{77} and so forth) must be made for either kind of log.

LISTING:

```
Step       Entry       Step       Entry       Step      Entry

000        *LBL        020        HALT display F
001        A                      ÷           050       HALT
002        RC1         030        RC1                   display M
           0                      0                     STO
           8                      9                     1
           X                      =                     1
           HLT key in depth       *log        060       RC1
           +                      ÷                     0
           RC1                    RC1                   4
           0                      0                     X
010        6                      5                     HALT key
           = formation temp.      =                     in Ro
           STO         040        +/-                   ÷
           0                      INV                   7
           4                      *log                  7
           X                      HALT display 0        ÷
           HLT key in Rxo         STO                   RC1
           ÷                      1           070       0
           7                      0                     0
           7                      *log                  =
020        ÷                      *1/x                  *1/x
           RC1                    X                     X
           0           050        RC1                   RC1
           1                      0                     0
           =                      0                     2
           STO                    *log                  =
           0                      =                     STO
           0                      +/-
```

```
Step      Entry         Step      Entry         Step      Entry

080       1             120       X
          2                       RC1
          HALT display ppm        1
          *LBL                    4
          B                       =
          HLT key in depth        X
          X                       RC1
          RC1                     0
          0                       9
          8                       =
090       +             130       HLT display SP log ppm
          RC1
          0
          6             Example:  Rmf77 = 1.0 Ohm-meter )
          +                       Surf. temp. = 90°F     )
          4                       G = .01 F°/foot        )
          6                       D = 4460 feet          ) INPUT
          0                       Rxo = 9.0 ohm-meter    )
          =                       Ro = 6.0 ohm-meter     )
          X                       SSP = -15.0 millivolts)
100       RC1                     F   = 15.73             )
          1                       Ø   = 0.22              )
          3                       m   = 1.8               )
          =                       ppm = 9000, resistivity) OUTPUT
          *1/x                                log         )
          X                       ppm = 11339, SP log     )
          5
          3
          7
          X
110       HALT key in SSP, a neg. #
          =
          INV
          *log
          X
          RC1
          0
          1
          =
          *1/x
```

ABSTRACT

STATUS REPORT, RAFT RIVER PROJECT SAMPLING, ANALYSIS, AND ENVIRONMENTAL EFFECTS STUDIES

A. C. Allen, J. M. Baldwin, R. E. McAtee
Allied Chemical Corporation, Idaho Falls, Idaho

This report describes sampling methods presently being used for the geothermal wells and associated effluents at the Raft River Geothermal site near Malta, Idaho. Analytical techniques used for species difficult to accurately determine are discussed. Also reported are the plans for the on-site laboratory under construction; including the analytical support it will provide.

The primary criteria for development of a sampling system was preservation of the environment of the sample source. Well samples were maintained at the well temperature and pressure until time of analysis or until the sample was cooled, depressurized, and diluted. Pressure cylinders are used to collect samples from sample sources with temperatures above the boiling point. Plastic bottles are used to collect from sample sources below the boiling point.

Chemical analysis problems mostly occur in sample preparation. Problem species discussed are $S^=$ and F^-. Sulfide ion requires special sampling and sample preservation techniques to obtain reliable analysis. Fluoride determinations are usually requested for the surface and the bulk of agricultural samples. The standard bulk analysis technique is not useful for grain samples, but ignition techniques appear promising. Chelating agents were used to remove surface F^-.

The laboratory being fabricated at the Raft River geothermal site will furnish limited analytical chemistry support. Analytical procedures will be limited to determining the concentration of major components since skilled chemical technicians will not be available. Trace element analysis and the large variety of environmental analysis will continue to be analyzed in the larger laboratories.

Introduction

Several techniques have evolved for sampling geothermal fluids. This is natural since the requirements vary from site to site. For instance, Union Oil's problem of sampling steam at the Geysers(1) is significantly different from the USGS problem of sampling springs(2) or of sampling hydrothermal resources, such as found at Raft River(3).

This report describes the sampling, analysis, and preservation techniques used by Allied Chemical Corporation at the Idaho National Engineering Laboratory (INEL) for the geothermal wells and associated effluents at the Raft River Geothermal Site near Malta, Idaho. It will describe some chemical studies performed at the site. The analytical support for experiments being performed at the geothermal site will be discussed. Also, this report will describe the analytical facility being constructed at the Raft River Geothermal Well #1 site, its present analytical support, and future direction.

The Raft River Geothermal Site is located in south central Idaho near the city of Malta. There are a number of hot water wells in the area in addition to the three geothermal wells drilled by Aerojet Nuclear Corporation. The three wells have been drilled to depths of 4989, 5988, and 5816 ft with bottom of the hole measured temperatures of 144°, 145°, and 144°C, respectively(4). Wells #1 and #2 had artesian flows of 600 and 800 gpm, respectively. Well #3 has not been tested. Also, Well #1 was drilled at the junction of two minor fault zones. Well #2 was drilled 3000 ft from Well #1 on one of the fault zones. Well #3 was drilled about 5000 ft away from the fault zone. The purpose of locating the wells this way was to assist in the geothermal water reservoir study. These wells are along the border of a large irrigation district. This would place a large cold water reservoir in the same area as the geothermal wells. If this cold water reservoir is the water source for the geothermal water, it could mean an almost unlimited source of geothermal water. It is this set of circumstances that appears to exist in many areas of Idaho's Snake River Plain that has caused such interest by geothermal developers. It would appear that this could be one of Idaho's major energy sources.

Sampling

The sampling technique used for hot pressurized fluid systems, such as the geothermal wells, was developed to preserve the sample environment as nearly as possible. Temperature change and interraction between the sample and the sample vessel walls are two variables encountered in stream, spring, and hot spring sampling. Pressure changes can cause chemical changes in samples from below the surface or from wells held under pressure. In order to minimize these problems, a sampling system was developed that would maintain pressure and temperature when the water sample was transferred to the sampler and transported to the place of chemical analysis. The system also includes a means to quench the sample by simultaneous cooling and diluting. This should be carried out just before analysis, but can be done prior to transit to an analytical laboratory.

The sampling system consists of three parts; the sample vessels, the storage oven, and the desampler. The sampler is a 304 stainless steel sample cylinder equipped with stainless steel valves and purge line, as shown in Figures 1 and 2. The equipment is similar to the evacuated cylinders described by A. Stoker(5). Some samplers are equipped with a stainless steel in-line filter holder. This unit used a 25mm diameter, 5-micron Teflon filter. Gas samples are collected in these samplers, but are not kept at well temperature. The oven is constructed for rugged use, as shown in Figures 3 and 4. It is a stainless steel box with three inches

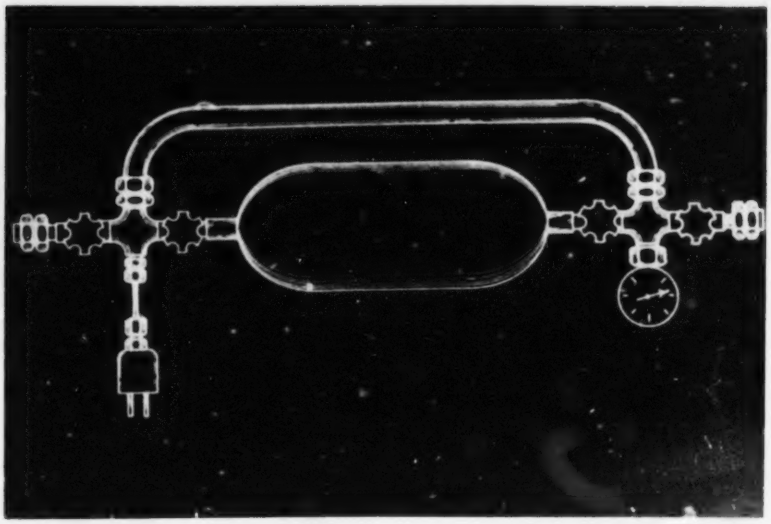


Figure 1. Geothermal high pressure sampler.

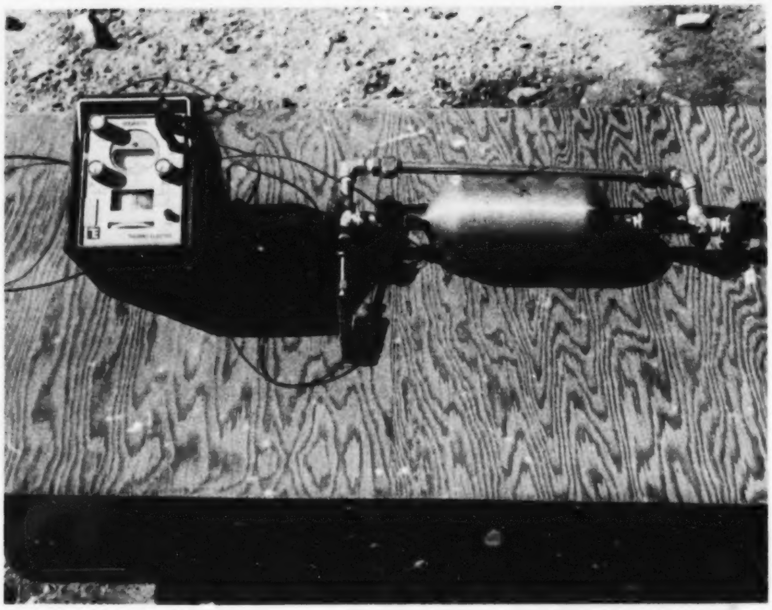


Figure 2. Geothermal high pressure sampler with temperature readout.

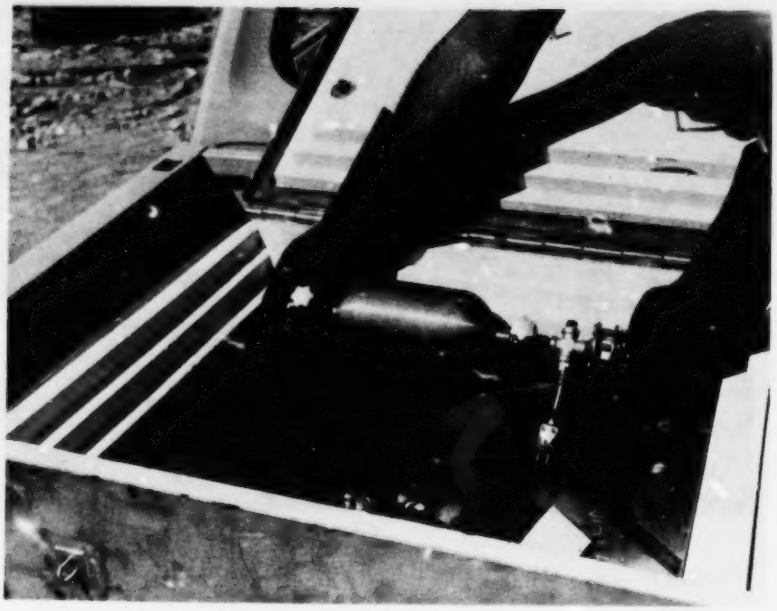


Figure 3. Sample storage oven.

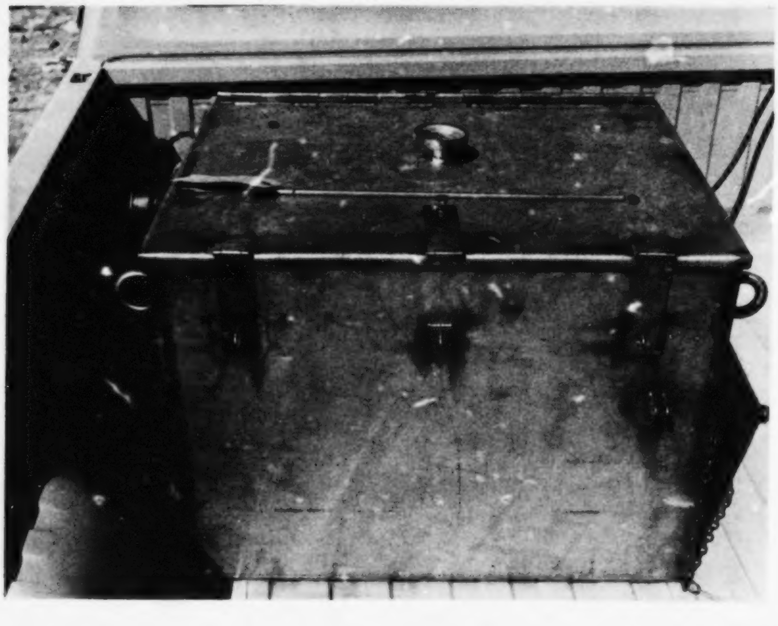


Figure 4. Sample storage oven.

of Marinite insulation, a stainless steel liner, and a 1100-watt heater. The desampler, shown in Figure 5, is used to cool and dilute hot pressurized geothermal fluid while keeping it at a pressure that will not allow phase separation. A nonreactive gas, such as helium or nitrogen, is used to pressurize the system. It can also be used to purge air or other reactive gases from the sample.

A study was made to determine the best approach to sampling and sample care in a pressurized fluid system. An evaluation of the following methods was made:

1) A pressurized sample kept at wellhead temperature and pressure until analysis time;
2) A pressurized sample treated with HCL and kept at wellhead temperature and pressure until analysis time;
3) A pressurized sample treated with HF and kept at wellhead temperature and pressure until analysis time;
4) A pressurized sample treated with NaOH and kept at wellhead temperature and pressure until analysis time;
5) A pressurized sample simultaneously cooled and diluted under pressure as quickly as possible after collection and stored in a plastic bottle until analysis time.

The results indicated that the reagent-treated samples caused interference problems and the analysis data were inconsistent.Whereby the samples kept at wellhead temperature and pressure and the samples cooled and diluted under pressure created few analysis problems and the data were consistent. However, it was noted that the sample stored at wellhead temperature until analysis did have more precipitate than the sample that was cooled and diluted under pressure and stored in a plastic bottle. Qualitative analysis of the filter solids collected, when the samples were

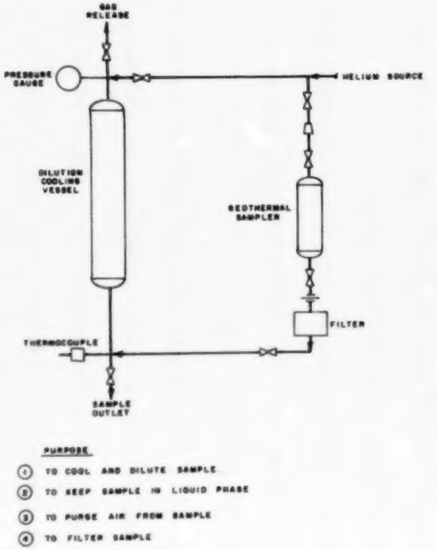

GAS RELEASE
PRESSURE GAUGE
HELIUM SOURCE
DILUTION COOLING VESSEL
GEOTHERMAL SAMPLER
FILTER
THERMOCOUPLE
SAMPLE OUTLET
PURPOSE
① TO COOL AND DILUTE SAMPLE
② TO KEEP SAMPLE IN LIQUID PHASE
③ TO PURGE AIR FROM SAMPLE
④ TO FILTER SAMPLE

Figure 5. Desampling apparatus.

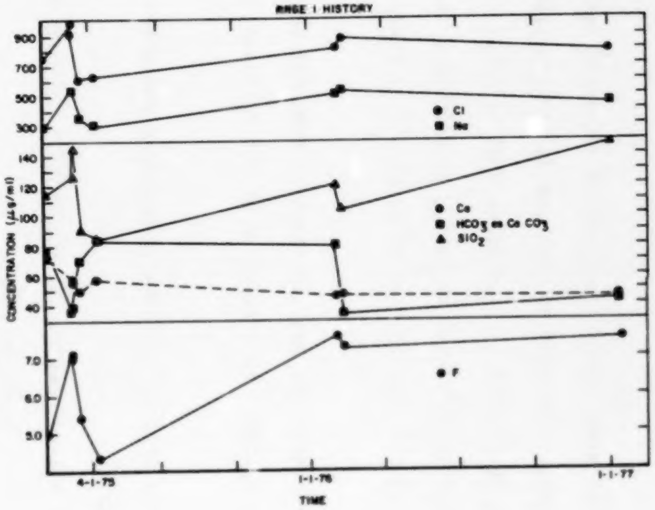


Figure 6. Raft River geothermal well # 1 chemical history.

filtered at the wellhead, shows Fe to be the major constituent. When the sample was not filtered and stored at wellhead temperature and then filtered, the major filter solids were Fe and SiO_2. Because of possible problems with SiO_2 losses, the method requiring immediate cooling and diluting under pressure was adopted.

Geothermal Site

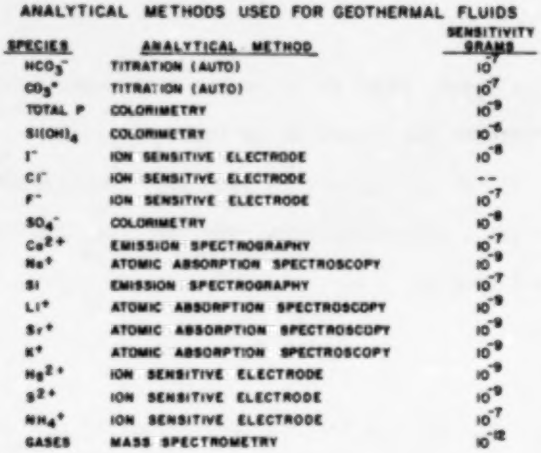
Samples from sources with temperatures below the boiling point are collected in plastic and glass bottles. The sample bottle material is selected according to the chemical species to be analyzed. Samples collected from water sources other than geothermal sources are treated according to the procedures described by E. B. Brown, M. W. Skougstad, and M. J. Fishman in Book 5, Chapter A-1 of the test, "Techniques of Water Resources Investigations of the United States Geologic Survey"(6).

Analysis

The problems encountered in the analysis of this geothermal water are typical of conventional water analysis. The geothermal water from the wells near Malta, Idaho is very low in dissolved solids compared to geothermal water from other areas. This results in reduced interferences during analysis. Consequently, for most chemical species, only small changes in existing methods of analysis were necessary. Table I lists the species, the method of analysis, and the method sensitivities.

Table II lists some of the purposes for the analysis of a particular species. This is only a partial listing showing some of the uses the chemical analysis, but it is apparent different activities require different sets of chemical knowledge. The most comprehensive demand for chemical information comes from environmental sources. Not shown in Table II, are

TABLE I. ANALYTICAL METHODS USED FOR GEOTHERMAL FLUIDS.



ANALYTICAL METHODS USED FOR GEOTHERMAL FLUIDS

SPECIES	ANALYTICAL METHOD	SENSITIVITY GRAMS
HCO_3^-	TITRATION (AUTO)	10^{-7}
$CO_3^=$	TITRATION (AUTO)	10^{-7}
TOTAL P	COLORIMETRY	10^{-9}
$Si(OH)_4$	COLORIMETRY	10^{-6}
I^-	ION SENSITIVE ELECTRODE	10^{-8}
Cl^-	ION SENSITIVE ELECTRODE	--
F^-	ION SENSITIVE ELECTRODE	10^{-7}
$SO_4^=$	COLORIMETRY	10^{-8}
Ca^{2+}	EMISSION SPECTROGRAPHY	10^{-7}
Na^+	ATOMIC ABSORPTION SPECTROSCOPY	10^{-9}
Si	EMISSION SPECTROGRAPHY	10^{-7}
Li^+	ATOMIC ABSORPTION SPECTROSCOPY	10^{-9}
Sr^+	ATOMIC ABSORPTION SPECTROSCOPY	10^{-9}
K^+	ATOMIC ABSORPTION SPECTROSCOPY	10^{-9}
Hg^{2+}	ION SENSITIVE ELECTRODE	10^{-9}
S^{2+}	ION SENSITIVE ELECTRODE	10^{-9}
NH_4^+	ION SENSITIVE ELECTRODE	10^{-7}
GASES	MASS SPECTROMETRY	10^{-12}

TABLE II. CHEMICAL INFORMATION REQUIRED BY DIFFERENT GEOTHERMAL DEVELOPMENT ACTIVITIES.

	Li	Na	K	Mg	Ca	Sr	Hg	As	SiO_2	F^-	Cl^-	S^-	$HCO_3^=$	$SO_4^=$	CO_2	O_2
Exploration		x	x		x		x		x	x	x		x			
Drilling		x	x		x				x				x			
Reservoir Eng.	x	x	x	x	x	x			x	x	x		x			
Equip. Design					x				x	x	x	x	x	x	x	x
Environmental	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Reinjection					x				x				x	x		
Research	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x

the frequency, speed of analysis, and accuracy required. These also vary from activity to activity. For instance, during well drilling only a few species need to be analyzed, but requests are likely to be frequent and rapid analyses are essential. Results for environmental purposes usually are not required quickly, but must be accurate with reliable statistics.

Sample Preservation Techniques

Sulfide ion determination is a problem analysis requiring special sample preservation techniques. The sulfide losses appeared to result from the air oxidation of sulfide ion to sulfate ion. Zinc acetate and sodium carbonate were added to co-precipitate the sulfide ion. The sulfide ion was redissolved and the concentration determined by the ion selective electrode method. Samples were stored by this method of preservation for up to 7 days without appreciable sulfide losses.

Mercury ion is preserved by adding enough nitric acid to adjust the sample solution pH to 1. Sodium dichromate is added to eliminate any volatile mercury compounds.

For the remainder of the species present in the geothermal fluids, the only preservation technique used was sample dilution. In a study, using various concentrations of various acids to preserve certain species in the sample fluid, it was found that sample dilution resulted in data with better precision.

Special Chemical Studies

An experiment using the geothermal water from the Raft River Geothermal Well #7 for irrigation of a variety of grains and potatoes was performed. The analysis consisted of determining fluoride concentrations on the surface and within the grain and potatoes. Table III shows the results of the analysis.

TABLE III. FLUORIDE CONCENTRATIONS ON THE SURFACE OF AGRICULTURAL SAMPLES.

	Fluoride Conc. µg/ml
Triangle Dairy Potable Water Well	0.81
Triangle Dairy Warm Water Well	14.2
Erwin Potable Water Well	8.4
Erwin Stock Water Well	9.7
Erwin Irrigation Well	11.5
Udy Irrigation Well	2.0
BLM Hot Water Well	5.6
Cranks Hot Water Well	4.1
Raft River Geothermal Well #1	8.0
Raft River Geothermal Well #2	9.5
Raft River Geothermal Well #3	5.0
Cane Canyon Spring	< 0.4
Redrock Noll Spring	< 0.4
Cedar Noll Spring	< 0.4
Irrigation Well NE of Malta, Idaho	< 0.4
Raft River	0.8
Wytes Well	7.6

TABLE IV. FLUORIDE DATA FROM REGIONAL WELLS AND SPRINGS.

			Fluoride Concentration (µg/g)
	Sprinkled With Geothermal Water	Flooded With Geothermal Water	Sprinkled With Fresh Water
Barley	8.7	0.7	0.7
Wheat	32.	4.3	4.2
Oats	54.		8.9
Potatoes		0.1	0.07
		Total Fluoride Concentrations for Agricultural Samples	
Barley	14	16	4
Wheat	33	23	7
Oats	65		15
Potatoes		0.8	0.8

F^- concentration in geothermal water is ~9.5 µg/ml

F^- concentration in fresh water is ~2.0 µg/ml

The method for fluoride, suggested by Orion Laboratories(7) for total grain analysis, resulted in the grains forming a jelly-like substance that resisted analysis. A method involving ignition of the grain powder in a Ca_2O slurry was used. The method used to analyze the surface fluorides involved in the leaching of the samples with a complexer buffer solution consisting of citrate, triethylzmine, and sodium chloride. The fluoride concentration was determined by anion selective electrode. The standard addition method was used to check for interferences from the sample matrix.

Fluoride Concentrations of Regional Effluents

Although fluoride analysis of water samples required no special preparative or analytical methods, data from regional wells and springs have been tabulated in Table IV. This study did prove to be of interest due to the variation in fluoride concentration of regional effluent sources.

Ferric-Ferrous Ion Study

A study was made on the geothermal water taken from Raft River Geothermal Well #1 to determine the ferrous-ferric ion ratio. This study was necessary due to the lack of down hole sampling equipment and consequently, the ability to sample at the source of the geothermal fluid. It is believed that ferric ion comes from the fluid source, whereby, ferrous ion results from fluid reaction with the well casing and other down hole equipment.

The Hach DR-2 spectrophotometer at the well site was used for the analysis. The ferrous ion concentration was determined colorimetrically by developing the characteristic yellow color of ferrous ion complexed with O-phenanthroline. Then, hydroxylamine was added to reduce ferric ion to ferrous ion and the total ferrous ion concentration determined. The difference represents the ferric ion concentration. The ferrous ion concentration in the geothermal fluid was determined to be 0.100 ± 0.004 ppm. Ferric ion content was below the limit of detectability. It is probable that most of the iron in the fluid originates from the casing and other ferrous materials dropped into the well during drilling and logging operations.

New Temperature Predictions at Raft River

Geothermometry calculations from Raft River Geothermal Well samples predict aquifer temperatures up to 188°C. Maximum measured bottom hole temperatures have been about 146°C which probably indicates the major geothermal aquifer has not yet been tapped. Both geothermometers employed show higher aquifer temperatures for RRGE2 than for RRGE1. See Table V.

The SiO_2 and Na-K-Ca geothermometers remain the most reliable indicators of aquifer temperature(8,9). The SiO_2 thermometer depends on the

TABLE V. ANALYTICAL DATA AND PREDICTED TEMPERATURE FROM RAFT RIVER WELLS.

Well	Sample # -Pres. (psi)	Date Sampled	SiO$_2$(ppm)	Ca (ppm)	Ca (mol)	Na (ppm)	Na (mol)	K (ppm)	K (mol)	SiO$_2$ Temp. °C	Na-K-Ca Temp.°
RRGE1	1.27f*	3-23-75	94	50	1.25x10^{-3}	350	.0152	25	6.39x10^{-4}	125	169
RRGE1	2-160	3-23-75	88	52	1.3 x10^{-3}	368	.016	25	6.39x10^{-4}	125	167
RRGE1	2-125	4- 4-75	73	56	1.4 x10^{-3}	307	.0132	21	5.37x10^{-4}	100	164
RRGE1	3-125	4- 4-75	66	56	1.4 x10^{-3}	305	.0133	21	5.37x10^{-4}	100	164
RRGE2	2-125	7- 9-75	148	36	9 x10^{-4}	355	.0154	35	8.95x10^{-4}	165	190
RRGE2	5-115f	7- 9-75	169	38	9.5 x10^{-4}	368	.016	43	1.09x10^{-3}	170	199
RRGE2	6-110f	7- 9-75	165	37	9.25x10^{-4}	373	.0162	38	9.72x10^{-4}	170	193
RRGE2	10-108	7- 9-75	143	38	9.5 x10^{-4}					160	
RRGE2^{+}	1 ~ 120f	7-17-75	175	40	1 x10^{-3}	387	.0168	33	8.43x10^{-4}	175	182
RRGE2^{+}	2 ~ 120f	7-17-75	165	40	1 x10^{-3}	391	.017	37	9.46x10^{-4}	170	188
RRGE2^{+}	5 ~ 120	7-17-75	128	37	9.25x10^{-4}	397	.0173	33	8.43x10^{-4}	132	189
RRGE2^{+}	6 ~ 120	7-17-75	148	41	1.025x10^{-3}	390	.017	35	8.95x10^{-4}	165	185
RRGE2	4-115	7-24-75	152	38	9.5 x10^{-4}	394	.0171	34	8.69x10^{-4}	165	184
RRGE2	5-110	7-24-75	152	40	1 x10^{-3}	385	.0167	34	8.69x10^{-4}	165	184
Crank		10-18-74	88	125	3.12x10^{-3}	1082	.0470	32	8.18x10^{-4}	125	138
BLM		10-18-74	83	54	1.35x10^{-3}	534	.0232	20	5.11x10^{-4}	125	144

*Samples filtered before collection

+Samples maintained at collection temperature till just before analysis solubility of quartz as a function of temperature. The Na-K-Ca thermometer is an empirical calculation based on exchange reactions of the feldspars. Raft River solutions chemically align closely with other geothermal water of rhyolitic origin. Since rhyolites are composed of primarily orthoclase (K-feldspars), quartz, and plagioclase (Na-Ca feldspar solid solution) both geothermometers should apply. Application of this thermometer to Raft River Geothermal Wells predicted higher than measured temperatures.

The Na-K-Ca thermometer predicts substantially higher temperatures than the SiO_2 thermometer. Except for samples collected on 7/17/75, the samples were cooled to ambient temperature following collection. This may be sufficient to precipitate some amorphous silica, thus reducing the silica content in solution. Filtered samples show higher SiO_2 content than the unfiltered samples and this probably reflects reaction with iron oxides entrained from the casing. Qualitative analysis of filter samples shows Fe to be the major constituent and solids filtered just prior to emmission spectroscopy show both Fe and Si to be major components. Because of the likely problems with SiO_2 precipitation, the temperature predicted by the Na-K-Ca geothermometer is likely to be more accurate. The possible exception is the filtered samples collected on 7/17/75 which predict temperatures of 170° and 175°C.

These data indicate higher aquifer temperatures than those thus far encountered. The temperatures predicted by the shallow Crank and BLM Wells are lower due to continued reaction during transit in the rock . For the same reason, the higher temperatures predicted by the geothermometers indicate the wells may not yet be near the maximum aquifer temperature.

TABLE VI. AVERAGE CONCENTRATION VALUES FOR SPECIES ANALYZED AT THE RAFT RIVER GEOTHERMAL WELLS.

Well History of the Raft River Geothermal Wells

The most important study of a geothermal well is its chemical history from the time of completion. The routine analysis of dominant species over this period develops a record concentration. Once the magnitude is known and trends established, it can assist in predicting more accurately source temperature, corrosion, and deposition rates in well and power producing equipment, the rate of well depletion, and many other determinations of importance in the geothermal well development. Figures 6, 7, and 8 show the variation of Ca^{++}, $CaCO_3$, SiO_2, Cl^-, F^-, and Na^+ concentrations over the sampling period of each well.

Table VI shows the average value for the concentration of the listed chemical species.

SPECIES	WELL RRGE-1 CONCENTRATION (PPM)	WELL RRGE-2 CONCENTRATION (PPM)	WELL RRGE-3 CONCENTRATION (PPM)
HCO_3^-	77	40.9	53
NH_4^+	2.5	0.51	0.47
TOTAL P	0.012	0.02	0.25
$Si(OH)_4$	162	212	193
I^-	0.036	0.021	0.24
Cl	717	682	2001
F^-	5.6	8.6	4.3
SO_4^-	61	55	32
Ca^{2+}	56	38	193
Na^+	403	383	1156
TOTAL Si	44	70	67
Li^+	1.3	1.04	3.1
Sr^+	1.5	1.04	6.4
K^+	27	36	91

TABLE VI. AVERAGE CONCENTRATION VALUES FOR SPECIES ANALYZED AT THE RAFT RIVER GEOTHERMAL WELLS

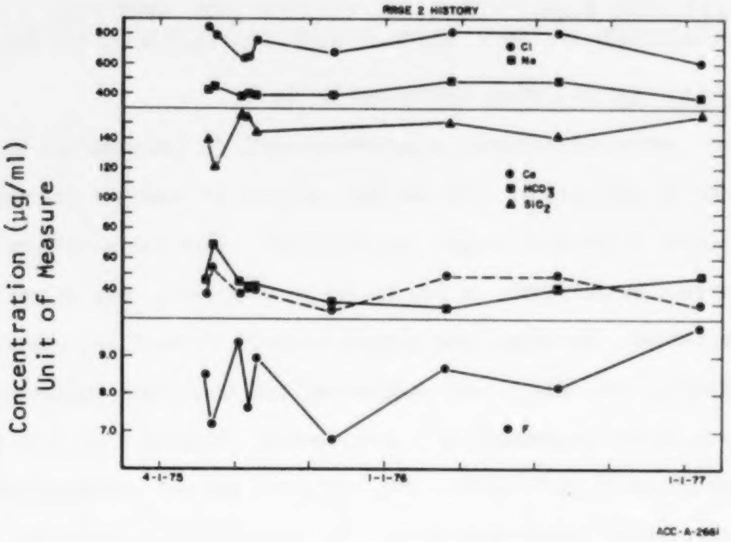


Figure 7. Raft River geothermal well # 2 chemical history.

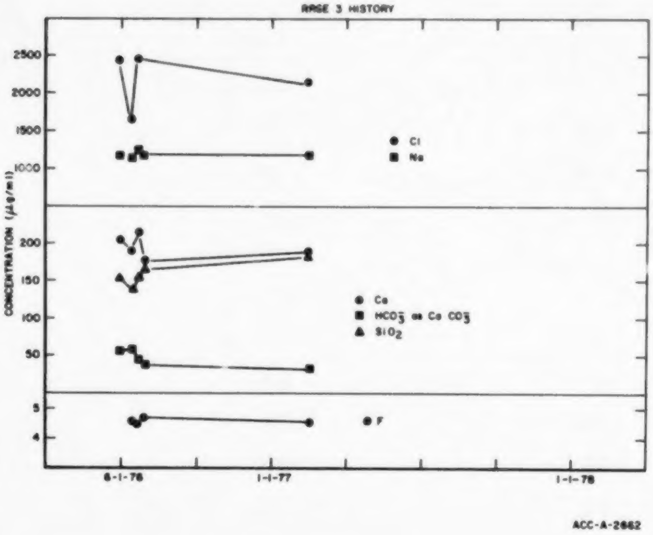


Figure 8. Raft River geothermal well # 3 well history.

Research Programs at the Raft River Geothermal Site

A number of experiments have been, or are being performed at the Raft River Geothermal Site. These include the following:

1) Fluidized bed heat exchanger study for the control of scale on heat exchange surfaces.
2) Direct contact heat transfer experiments.
3) Agricultural experiments using geothermal water to irrigate a variety of grains and vegetables.
4) Corrosion study of materials for power plant components.
5) Experiments to determine the feasability of using treated geothermal water in cooling tower applications.
6) Fish farming study to determine growth and effects of geothermal water on fish.

On-Site Analytical Chemistry Laboratory

The experimental use of the Raft River Geothermal Site has been mentioned to show the need for many on-site chemical analysis. On-site chemical analysis are required for:

1) monitoring of selected chemical species required for well histories,
2) environmental monitoring and studies,
3) reservoir and well evaluation,
4) experimental support, and
5) analysis of unstable chemical species that cannot be stored for transport to off-site laboratories.

This facility is being assembled at the Raft River Geothermal Site. The laboratory will contain an atomic absorption spectrophotometer, a colorimetric spectrophotometer, an automatic titrator, a gas partitioner, a specific ion meter, electrodes, and a number of pH, salinity, and conductivity meters. The greatest limitation is the lack of trained personnel. Once they are available, the laboratory will be capable of a broad spectrum of analyses.

In-Line Monitoring Programs

Plans have been initiated for the installation of monitoring equipment for in-line measurement of pH, oxidation-reduction potential, and conductivity at the geothermal wellheads. Equipment has been ordered and installation will take place upon shipment of this equipment. The monitoring will be possible because pH, ORP, and conductivity probes designed for 125°C temperatures and 150-psi pressure are avaliable. This equipment is designed and manufactured by Balsbaugh Inc. This system, we hope, will signal changes in well composition. Researchers at Battelle Northwest in Richland, Washington are working to develop probes for conductivity and oxidation-reduction potential that will withstand higher temperatures and pressures so monitoring systems of this type can be extended to other geothermal sites.

Conclusions

1. After testing several sampling techniques we adopted collection under pressure followed by simultaneous cooling and dilution under pressure. This technique prevents errors due to phase separation and minimizes the hazard of deposition on walls of the sample container. Samples kept hot until analysis time sometimes contained precipitates high in SiO_2 and iron.
2. An ignition technique for fluoride in grain was developed.
3. A sulfide ion preservation technique was developed so samples could be analyzed several days following collection.

4. Well composition for the three geothermal wells were plotted as a function of age. Most components gyrated wildly during the first few months following drilling then settled into a concentration range with much smaller deviations.
5. The need for on-site chemical analysis was documented. A laboratory is being constructed. Typical of remote geothermal locations the limit on laboratory capabilities will be imposed by the lack of trained personnel.

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BOREHOLE GEOPHYSICAL LOGGING AS COMPLEMENT TO GEOTHERMAL WELL EFFLUENT SAMPLING

S. K. Sanyal and R. B. Weiss
Geonomics, Inc., Berkeley, California

ABSTRACT

Sampling and analysis of well effluents is an important means of detecting ground water pollution. There are, however, some drawbacks in this technique. If water is sampled from an uncased (open hole) well, the water represents a mixture of water from various permeable layers, rather than from an individual layer. This is an undesirable situation if water quality varies significantly from layer to layer. If the water is sampled from a cased well, the sample represents only the layers at the depths of well completion. One way of obtaining a continuous vertical profile of water quality with depth is to apply geophysical borehole logging to complement well effluent sampling and analysis, in both open and cased holes. Both real and hypothetical examples are given to illustrate the potential role of borehole geophysical logging in pollution monitoring.

Geophysical Well Logs in Water Quality Studies

In order to evaluate the possibility of ground water pollution, one has to assess the qualities of both the shallow ground water and the geothermal water. The most direct means of assessing water quality is by chemical analysis of the water sample. However, water sampling from wells can be complicated by several factors as discussed below.

Both shallow ground water and geothermal water occur in a sequence of porous and permeable rock layers alternating with impermeable layers (Figure 1). If water is sampled from an uncased (open-hole) well, the water represents a mixture of water from various permeable layers, rather than from an

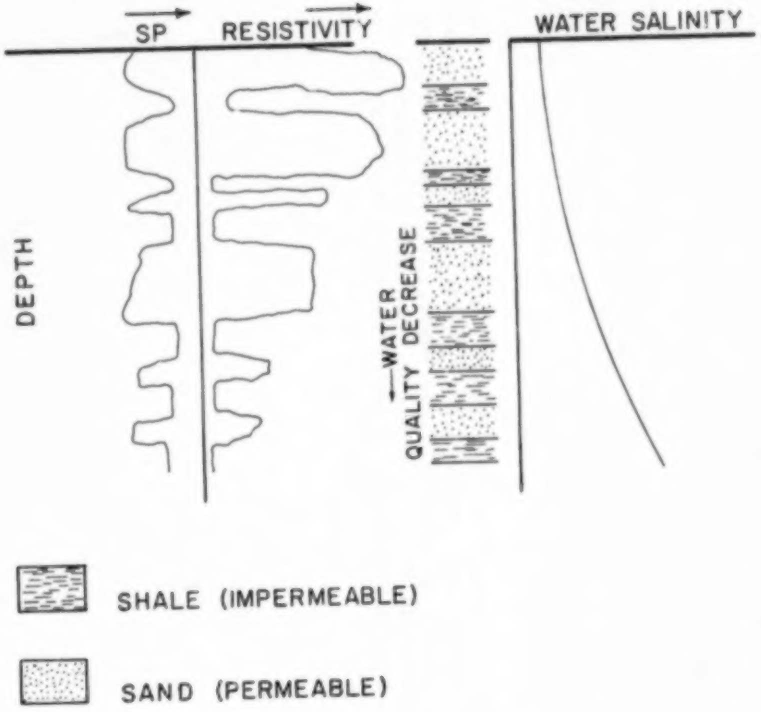
SP
RESISTIVITY
WATER SALINITY
DEPTH
WATER QUALITY DECREASE
SHALE (IMPERMEABLE)
SAND (PERMEABLE)

Figure 1. Vertical profile of water quality from well logs.

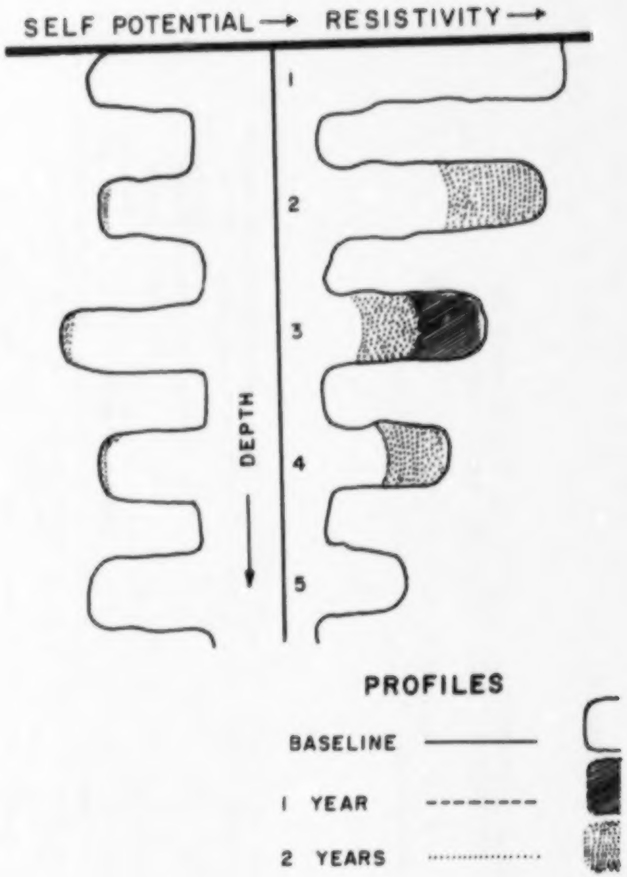
SELF POTENTIAL →
RESISTIVITY →
1
2
3
4
5
DEPTH
PROFILES
BASELINE
1 YEAR
2 YEARS

Figure 2. Temporal changes in log response indicating change in water quality profile.

individual layer. This is an undesirable situation if water quality varies significantly from layer to layer. If water is sampled from a cased well, sampled water represents only the layers at the depths of casing perforations. One way of obtaining a continuous vertical profile of water quality with depth is to use geophysical borehole logging techniques. For example, after a well is drilled and before it is cased, electrical and self-potential logs are normally run (simultaneously) in the well. A careful analysis of these logs permits calculation of water conductivity versus depth. If sodium chloride is the predominant dissolved constituent, the parts per million of the total dissolved solids can be calculated from the conductivity. If large amounts of other dissolved compounds are present, one can calculate an "equivalent" NaCl concentration in the water. If the chemical analysis of a water is known, an equivalent NaCl concentration can be calculated by using standard charts. The primary importance of using well logs is to obtain a vertical profile of the relative amounts of total dissolved solids without the need for sampling. Such a profile serves as the baseline data against which temporal changes in water quality can be evaluated. Figure 1 shows a case where water salinity increases with depth as inferred from the well logs. By repeated logging of a well at regular intervals, any temporal change in water quality can be detected.

Figure 2 illustrates a temporal change in water quality as monitored by well logging. Here, after one year, layer 3 shows evidence of contamination by saline water, while the other four layers preserve their original quality. After 2 years, the third layer shows further deterioration in quality, while layers 2 and 4 have begun to be contaminated. Thus, unlike monitoring by sampling and chemical analysis, the proposed technique not only indicates changes in water quality but also identifies the exact depths of contaminated layers and the degree of contamination in each layer.

If the wells are uncased, electrical resistivity and SP logs can be used for such monitoring. If the wells are cased, these logs cannot be used. In such situations, we recommend monitoring by pulsed neutron logging. If the porosity of a formation is known (from core data or other logs), salinity of the formation water can be calculated from a pulsed neutron log. Unlike electric logs, this log is not affected by the presence of casing around the borehole. Both these logs can be used to monitor water quality more effectively if used in conjunction with water sampling. Chemical analysis of a few water samples can be used to "calibrate" the proposed monitoring technique. Pulsed neutron logging can be used to detect changes in the concentration of certain special elements (e.g., boron, lithium) in formation water. These elements have very large neutron capture cross sections and consequently are easily detected by this log. Temperature logs may be used to monitor the movement of a contaminant, which is either hotter or cooler than the aquifer. Disposal of geothermal waste water can be monitored by this method.

Monitoring of the Contaminant Front

It is important to monitor the entire profile of water quality in a well particularly if there is a large variation in permeability of the various layers. Waste water disposed of in a well will travel faster through the more permeable layers (e.g., layer 3 in Figure 2). Thus, the surface of contact between contaminated and uncontaminated water will not be uniform (by any reckoning). Reservoir engineering calculations can be applied to monitor and predict movement of this complex boundary. Molecular diffusion and mechanical dispersion make this boundary even more complex. Reservoir engineering techniques can be applied to evaluate diffusion and dispersion. Figure 3 shows a hypothetical disposal problem. By monitoring the water quality profile (calculated from logs) in the observation well, one can infer the movement of the contaminated water front. Such a monitoring technique can provide sufficient forewarning so that water wells can be saved from contamination. The disposal activity may be stopped or the producing wells may be selectively re-completed in layers safe from the advancing contaminated water.

Similar non-uniformity in the advance of contaminated water is also seen in the areal sense. This non-uniformity is caused primarily by the areal variation in formation permeability as well as the production characteristics of other wells in the aquifer. Reservoir engineering calculation techniques can be applied to monitor and predict the areal advance of the contaminated water. Figure 4 illustrates such a situation. The observation wells not only provide vertical definition of the advancing front but also the areal definition.

Thus, a judicious combination of well-logging, water sampling and concurrent reservoir analysis will be the most effective water quality monitoring scheme. Log monitoring can be done in observation wells (such wells will not be produced) as well as producing or injection wells. If the well is not cased, an electrical log can be used for monitoring. For steel-cased wells pulsed neutron logging should be used. However, a well can be cased with fiber glass casing

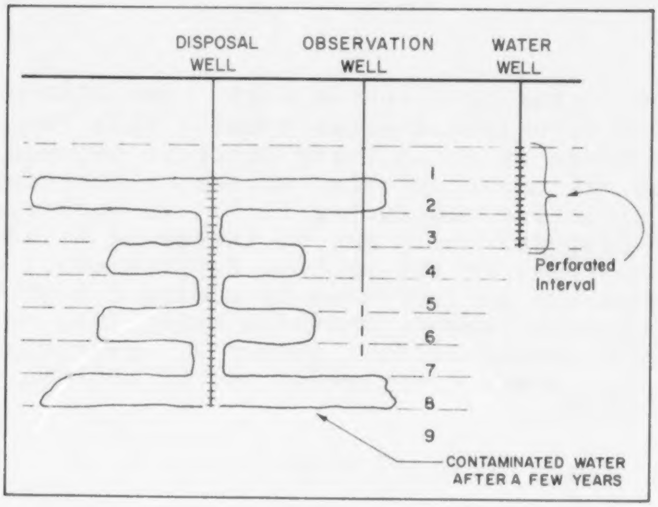
DISPOSAL WELL
OBSERVATION WELL
WATER WELL
1
2
3
4
5
6
7
8
9
Perforated Interval
CONTAMINATED WATER AFTER A FEW YEARS

Figure 3. Vertical conformance of the contaminated water front.

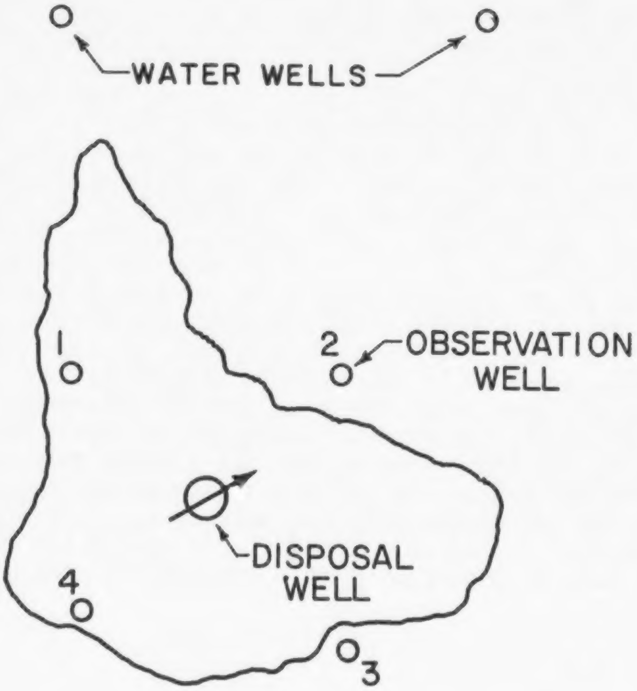
WATER WELLS
1
2
OBSERVATION WELL
DISPOSAL WELL
4
3

Figure 4. Areal spread of contaminated water.

to allow for monitoring by electric logs. Comparison with chemical analysis of selected water samples will improve log monitoring. If there is no salinity contrast between the contaminated and the uncontaminated waters, electrical logging will not be an effective monitoring tool. In such cases the salinity of the disposal water may be increased by adding a suitable inorganic salt or the neutron capture cross section of the disposal water may be increased by adding a high neutron capture cross-section element (provided water does not already have a significant amount of that element). Electrical logs can be used in the former case, while pulsed neutron log can be used in the latter.

Contamination Problems in Cased Holes

Aquifers may also be contaminated by the movement of contaminated water behind the casing. This is caused by differences in piezometric levels between various aquifer layers. Fluid migrates from a higher pressure to a lower pressure one through cracks or channels in the cement between the casing and the formation. Such flow behind casing in a disposal well may contaminate a shallow aquifer without being detected. Sometimes such flow causes deposition of radioactive salts behind casing after several years of flow. A gamma ray log run in the well will detect this anomalous radioactivity. By comparing gamma ray logs run in the same well at various times, one can often detect flow behind casing. In the extreme case, flow behind casing may create holes in the casing due to corrosion. Injected disposal water may escape into shallow ground water aquifer and contaminate it. A hole in the casing can sometimes be inferred from an anomalous increase in gamma ray intensity at a certain depth. However, this technique may not be definitive in all areas. On the other hand, SP log inside a cased hole is sensitive primarily to corrosion effects in the casing itself. Hence, changes over time of the SP response inside cased holes are likely to reveal zones of active corrosion. Gamma ray logging is inexpensive and is always run together with pulsed neutron logs. If pulsed neutron is used for monitoring, it may be monitored for any anomalous change in gamma ray intensity. Temperature logs (regular or differential) can be used to detect a variety of flow-behind-pipe problems.

ABSTRACT

USE OF RADIOACTIVE TRACERS IN GEOTHERMAL OPERATIONS

O. Vetter, Vetter Assoc., Laguna Beach, California

Tritium in form of tritiated water (THO) is the most suitable isotope for tracing the liquid water or steam in the field. It will follow the water (in the brine) through all phase changes as opposed to any other tracer. Some possibilities to use THO in reservoir evaluations in steam - or liquid - dominated reservoirs are outlined. Of particular interest is the precise determination of the reservoir recharge through injection wells. Qualitative and quantitative data can be obtained. Conclusions can be drawn as to the numbers, size, direction and conductivity of fractures and/or high permeability streaks. Pros and cons for the use of THO are given.

Other radioactive isotopes can be used to supplement conventional analytical measurements to solve some of the unique problems in geothermal operations. Pb-210; Zn-65; Ag-110 and etc., are perfectly suited to determine the behavior of the equivalent non-radioactive elements with an accuracy not possible by using conventional analytical techniques. Measurements of scaling tendencies and material balances are a few examples.

Radioactive isotopes can also be used to determine chemical or hydrodynamic data through the steel of pipes, vessels, etc. Velocities and flow rates of steam vs. brine, scale formation and flash percent are described as examples.

THE LBL GEOTHERMAL BRINE DATA COMPILATION PROJECT

Steven R. Cosner and John A. Apps

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

Data on geothermal fluids from the principal geothermal resources in the United States are being compiled at the Lawrence Berkeley Laboratory. The data collected are stored on a computer system to facilitate selective retrieval and manipulation. Printed copies of the compilation will be available with documentation from the laboratory as report LBL 5936.

The U. S. Energy Research and Development Administration has funded a project at Lawrence Berkeley Laboratory to collect and compile data on geothermal fluids for the principal geothermal resources in the United States. The project will contribute to a geochemical engineering program designed to overcome major technical problems related to the development of geothermal resources for both electrical and non-electrical uses.

The data compiled are stored on a computer filing system used at Lawrence Berkeley Laboratory. The compilation will be used to make statistical evaluations of geothermal fluids, and to compare the analyses with thermodynamic equilibrium models. The compilation is available to scientists and others interested in geothermal energy utilization.

The compilation covers all available data from geothermal wells in the United States with temperatures above 90 degrees Celsius, but excluding dry steam wells. Data from the Cerro Prieto geothermal field in Mexico are included due to its geographic proximity and geologic similarity to the Imperial Valley geothermal areas in California. Since the project is designed to aid research and development of the major water dominated geothermal resources, the compilation excludes dry steam and low temperature geothermal data. Private industry has proved the success of dry steam utilization. Hot spring data are being collected by the U. S. Geological Survey in Reston, Virginia, using the GEOTHERM computer system.

Data have been collected and compiled for the geothermal areas listed in Table 1. Wells have been drilled in a number of other areas, but fluid chemistry data from the wells are not available.

Table 1. Geothermal areas from which fluid chemistry data have been compiled.

California

- Salton Sea
- East Mesa
- Heber
- Mono-Long Valley

Idaho

- Raft River

Baja California, Mexico

- Cerro Prieto

Nevada

- Beowawe

New Mexico

- Baca Location No. 1*

Utah

- Roosevelt Hot Springs

* Baca Location No. 1 KGRA is same area as Valles Caldera.

The sources of most of the data are the published literature, and reports published by government agencies and national laboratories. Other sources are private well operators. It has been difficult and many times impossible to obtain comprehensive data from larger companies who own geothermal wells.

The data are stored on the Berkeley Database Management System, or BDMS. With BDMS, databases may be built easily using data elements or categories of storage tailored to the data being compiled. The computer system facilitates selective data retrieval and manipulation, editing and updating, and addition of new data. The system automatically maintains indices to the information to aid in retrieval and manipulation once the data are compiled.

The compilation of geothermal data has over fifty storage categories or data elements as shown in Table 2.

Figure 1 is a computer printout of a typical record of compiled data. The computer system is designed to print only the data present, with no extra space left for absent data.

For a few geothermal wells there are a number of fluid analyses published. In these cases all the data are compiled with multiple record listings for each well. There is usually a wide variation of constituent concentrations among samples from a single well, so the analysis considered best is given as the first listing for the well.

It has been observed during the compilation project that the units of concentrations in fluids are treated carelessly. The compilation gives the units used by the source, whether they are parts per million by weight, milligrams per liter, or something else.

A bibliography of all the sources of information used in the fluid data file has been maintained. This bibliography will also be stored on the BDMS computer system. Computer storage on BDMS allows computer searches for articles which discuss specific topics. To aid in the computer search, descriptors or key words are assigned to each article.

A bibliographic printout is shown in Figure 2. The entry at the upper right of the printout denotes the principal author and year of publication of the report. This entry corresponds to the bibliographic source given in the fluid data printout. The bibliographic printout also lists the descriptors to help a reader determine the subject matter of the report.

Once all the available data are compiled, evaluations of geothermal fluids will be made. Where sufficient data are available, the analyses will be checked for accuracy using thermodynamic equilibrium models. Temperature vs. concentration diagrams for the common elements can be made to help characterize the geothermal effluents. Evaluation of the

Table 2. Data elements, geothermal fluid data file.

Basic Information

- Well name
- KGRA or geothermal field
- Location
- County
- State
- Country

Well Information

- Well owner
- Lessee
- Drilling company
- Date drilled

Well Data

- Well depth
- Temperatures
  - Depth of temperature readings
- Pressure, shut-in
- Flow rates, pressures
- Production interval
- Reservoir lithology
- Production interval

Brine Information

- Sample type
- Sample date
- Sample number, laboratory
- Sample location
- Sampling method
- Condition of Sample
- Condition of well during sampling

Physical Data

- pH
  - Range of readings
  - Temperature of pH reading
- Electric potential
  - Temperature of reading
- Specific gravity
  - Temperature of reading
- Specific conductance
  - Temperature of reading
- Viscosity
- Total dissolved solids
  - Residue on evaporation or sum?
- Total alkalinity
- Other measurements

Brine Data

- Method of analysis
- Error limits
- Units
- Constituent name
  - Concentration
  - Other note (trace, errors, etc.)

Bibliographic Data

- Sources

```
                                  RECORD  56
                                  CODE NAME=SINCLAIR 4A
                                  SAMPLE TYPE=VATER
VELL SINCLAIR 4
SALTON SEA KGRA
LOCATION-- T12S, R13E, SEC. 4, 400FT N, 200FT E, FROM S QTR.COR.
IMPERIAL COUNTY, CA., USA

VELL INFORMATION
  OVNER-- GEOTHERMAL ENERGY AND MINERAL CORP.
  DATE DRILLED-- 25 APR 64 - 4 JUN 64

VELL DATA
  DEPTH -----  1617 METERS
  TEMPERATURE   255 C AT VELLHEAD
  PRESSURE, SHUT-IN-- >445 PSIG.

SAMPLING INFORMATION
  DATE-- 3 APR 75
  SAMPLE NUMBER, LABORATORY-- SAMPLE 6THS, LAVRENCE LIVERMORE LAB.
  SAMPLE LOCATION-- 25FT FROM VELLHEAD
  SAMPLING METHOD-- SAMPLING PROBE INSERTED INTO TOP PORTION OF 6
       IN. PIPE, COLLECTED UNDER PRESSURE INTO TEFLON-LINED
       STAINLESS STEEL BOTTLE.
  CONDITION OF SAMPLE-- SAMPLE TEMP=210 C, SAMPLE PRESSURE=220
       PSIG.  SAMPLE NOT COOLED DURING SAMPLING.
  CONDITION OF VELL DURING SAMPLING-- FULL FLOV THROUGH 6 IN. PIPE.

PHYSICAL DATA
  PH= 5.10    - - - - - - -     TEMP DURING READING= AMBIENT
  ELECTRIC POTENTIAL=   .160 VOLT.    TEMP DURING READING= AMBIENT
  TOT DISS SOLIDS=    291.00 G/L, SUM
                 =    300.00 G/L, RESIDUE ON EVAPORATION
  OTHER DATA--
  DENSITY= 1.22 AT 25 C.
  ENTHALPY= 210 CAL/G.
  COMMENT-- PH AND EH VALUES TAKEN ON SAMPLE PRESSURIZED BY GAS
       COLLECTED VITH SAMPLE.

BRINE DATA
  METHOD OF ANALYSIS-- RECONSTRUCTED ANALYSES--CALCULATED FROM
       LIQUID AND SOLID PHASES IN SAMPLE.
  ACCURACY OF ANALYSIS-- 5 PERCENT, EXCEPT NA AND AG--10 PERCENT;
       AL--1 PPM; S POSSIBLY LOV BY A FACTOR OF 2 OR 3.
  UNITS-- MG/L

  CONSTI-    CONCEN-
   TUENT     TRATION    COMMENT
  -------  ----------- ---------------------------------------
  SI           278
  NA         64000
  K          14700
  CA         30400
  MG            76
  CL        179000
  AG             0.7
  AL             5
  CU             3.3
  FE          1600
  MN          1310
  PB           111
  S             14
  CONCENTRATIONS NOT CORRECTED FOR STEAM LOSS.

BIBLIOGRAPHIC DATA
  SOURCES--
   HILL 75
   VITHAM 76
   HELGESON 68
   MUFFLER 69
```

Figure 1. Computer printed output of compiled data.

abundance or scarcity of information may lead to suggestions for further data collection efforts.

```
                                                    HILL 75

TITLE-  SAMPLING A TWO-PHASE GEOTHERMAL BRINE FLOW FOR
      CHEMICAL ANLAYSIS.

AUTHOR-  HILL, J.H.;MORRIS, C.J. [CALIFORNIA UNIV.,
      LIVERMORE (USA). LAWRENCE LIVERMORE LAB.].

REFERENCE-  SAMPLING A TWO-PHASE GEOTHERMAL BRINE FLOW
      FOR CHEMICAL ANALYSIS.  UCRL-77544, CALIF.
      UNIV., LLL, LIVERMORE, CALIF., (5 DEC 1975),
      27P.

DESCRIPTORS-  SALTON SEA KGRA; GEOTHERMAL BRINES;
      SAMPLING METHODS; CHEMICAL ANALYSIS; GEOTHERMAL
      WELLS; TWO-PHASE FLOW.
```

Figure 2. A computer-produced bibliographic listing.

It is the intent of this project to make the compilation as complete as possible. Therefore, anyone who has information or data on fluids from geothermal wells is sincerely requested to send the data to the authors. Contributions of current data are necessary to maintain the compilation as a useful tool aiding in geothermal energy development.

At this point the fluid data compilation is available as an easily readable computer printout. It will be published later by Lawrence Berkeley Laboratory as report number LBL-5936.

ABSTRACT

ANALYSIS OF TRACE CONTAMINANTS IN LOW TO MEDIUM SALINITIES GEOTHERMAL FLUIDS

K. Y. Chen
Environmental Engineering Program
University of Southern California
Los Angeles, California

Water samples from low to medium salinities KGRA were collected and analyzed for complete chemical composition, with special attention given to trace contaminants. The analytical determinations including speciation of redox species, for example, As(III) and As(V); partition between soluble and particulate fraction; as well as cations and anions balance.

Among a total of 49 geothermal water samples collected from California, Nevada, and Mexico, 56% of the samples exceed the maximum permissible concentration of 50 ppb arsenic for drinking water, while 83% of the samples exceed the recommended limits of 10 ppb. The concentration range for total arsenic is 0.5 to 3,006 ppb. Concentrations of As(V) range from 5 to 95% of total arsenic. 80% of the samples exceed the maximum permissible fluoride concentration of 1.3 ppm (79 to 90°F) for drinking water, with a range of 0.13 to 15.8 ppm. 98% of the samples exceed the recommended limiting concentration of 0.5 ppm boron for agricultural usage. The range was from 0.14 to 4.56 ppm. Ammonia and sulfide are significant contaminants in vapor dominant systems. In some cases, concentration of chloride, sulfate, and total dissolved solids may also present potential water quality problems. Trace metal concentrations are generally low and below the recommended drinking water standards.

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